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BUREAU OF MINES

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A CONVENIENT MULTIPLE-UNIT CALORIMETER INSTALLATION

BY

J. D. DAVIS AND E. L. WALLACE



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CONTENTS.

	Page.
Introduction	3
Essential features of a calorimeter	4
Bomb.....	4
Water jacket.....	5
Stirrer.....	5
Thermometer.....	6
Advantages and disadvantages of mercury thermometer.....	6
Graduation.....	7
Calibration.....	7
Apparatus used by the Bureau of Mines	8
The bomb.....	9
Gold plating.....	10
Calorimeter can.....	12
Stirrer.....	14
Lead wires.....	14
Constant-temperature bath.....	14
Temperature control of the bath.....	15
Device for handling water for the calorimeter.....	17
Temperature control.....	17
Measurement of water.....	17
Temperature measuring device.....	18
Repairing leaky thermometers.....	19
The bridge.....	20
Bridge first designed.....	21
Later design of bridge.....	21
Batteries for bridges.....	22
The galvanometer.....	22
Support for galvanometer.....	23
Distributor switch.....	24
Calibration of the bridge.....	24
Thermometer calibration.....	27
Method of calibration.....	29
Determination of the water value of the calorimeter.....	30
Calibration by combustion of standards.....	30
Electrical standardization.....	32
Apparatus needed.....	32
Results of standardization tests.....	34
Easy manipulation of resistance thermometer.....	35
Results with bureau's mercury thermometer.....	36
Performance of the calorimeter.....	37
Attainable rapidity.....	37
Constancy of jacket.....	37
Rate of combustion in the calorimeter.....	38
The cooling correction.....	40
Effect of evaporation.....	43

Apparatus used by the Bureau of Mines—Continued.	Page.
Accuracy attainable with the calorimeter.....	44
Important advantages of the equipment.....	46
Cost of the apparatus.....	46
Service obtained.....	47
Publications on the composition of coal.....	47

ILLUSTRATIONS.

PLATE I. A, Bomb, assembled; B, Details of bomb.....	Page.
II. Sections showing method of installing calorimeters	12
III. General view of calorimeter equipment.....	14
IV. Another view of calorimeter equipment.....	14
V. Switch for use with one bridge and galvanometer with three calorimeter equipments	24
VI. Details of control switch.....	24
FIGURE 1. Vertical cross section of bomb.....	9
2. Details of calorimeter.....	13
3. Device for regulating temperature in tank.....	16
4. Thermostat for temperature control of calorimeter water.....	17
5. Thermometer used in calorimeter.....	18
6. First bridge used.....	20
7. Improved bridge for calorimeter thermometer.....	21
8. Galvanometer suspension.....	23
9. Apparatus for electrical calibration.....	33
10. Curve showing variation in factor for bomb No. 3.....	35
11. Curves showing extent of temperature variations in jacket water in calorimeter tank.....	38
12. Combustion curve for naphthalene from results with bomb No. 3	41
13. Curves showing radiation corrections for bomb No. 3.....	43

A CONVENIENT MULTIPLE-UNIT CALORIMETER INSTALLATION.

By J. D. DAVIS and E. L. WALLACE.

INTRODUCTION.

Within the past ten years most purchasers of large quantities of coal have adopted the heat-unit basis of evaluation. The calorific value of a fuel, although it does not give all the information that could be desired as to quality, furnishes a more reliable specific indication than any other test that can be conveniently applied in the laboratory. The amount of heat a coal can produce on combustion is a main consideration in its purchase, and the heating value as determined in the laboratory is a direct and logical measure of that ability. Notwithstanding the fact that other important factors enter into the problem of coal evaluation, such as the use of coal suited to the equipment at hand or the character of heating desired, the calorific value is the best general expression of value, irrespective of the proposed use of the coal. It is therefore the most important factor to be considered in coal specifications. The Government early recognized this fact and is now buying the greater part of its fuel supply under specifications based on heating value.

The actual determination of the calorific value of a fuel should be carried out as cheaply as possible (as the price of coal limits the justifiable expense) and with a high degree of accuracy, in order to facilitate comparisons of coals not differing greatly in value. Here it may be said that as the sampling of coal is subject to an error of at least 1 per cent, it is useless to strive for higher accuracy in calorimetry. This objection, however, is not pertinent when the heating value is computed on the basis of coal free from moisture or ash, that is, the "coal substance." In other words, the chief cause of error in sampling is the taking of a sample that includes too small or too large a quantity of impurities to be correctly representative of the coal sampled, the sampling error as regards the character of the coal substance itself being small. Consequently, if the ash percentage is eliminated in computing the value of the coal as based on the calorimeter test, the sampling error is negligible. It is desirable that the accuracy attainable with a coal calorimeter be such that variations in determinations with duplicate samples shall not exceed

0.1 or 0.2 per cent, in order that there be a reliable means of differentiating between coals differing only slightly in value. Consequently, a high degree of refinement in apparatus and methods is essential. With some of the earlier types of calorimeters, and, in fact, with some apparatus now on the market, the actual accuracy attainable is less than that required.

ESSENTIAL FEATURES OF A CALORIMETER.

BOMB.

It is now generally recognized that the constant-volume type of oxygen bomb-calorimeter is required if more than a rough approximation of heating value is desired, and that for the best results an acid-proof bomb is necessary. The report of committee E-4 of the American Society for Testing Materials^a is clear as to this last point, the statement being made that "the bomb shall have an inner surface of platinum, gold, porcelain enamel, or other material which is not attacked by nitric or sulphuric acids, or other products of combustion." Parr^b has recently designed a bomb of an acid-proof base-metal alloy that is decidedly satisfactory. If the plating of a bomb is really acid-proof, a plated bomb, or an alloy bomb such as Parr's, is preferable to one with a replaceable lining. It is possible, of course, to so fit a lining that there will be no leakage between it and the corrodible metal, but it is difficult to keep the fit perfect in practice. Leakage in the replaceable lining type of bomb is not highly objectionable as regards the resulting decrease of accuracy, yet the fact that the life of the bomb is shortened by the resulting corrosion is important.

The fuel laboratory of the Bureau of Mines has not been successful in gold-plating steel bombs, but it is believed possible to procure a satisfactory coating by first plating with a base metal, such as copper or brass, then perhaps with nickel, and finally with gold.

The bomb should not be too heavy, a water value of about 500 being considered satisfactory. The chief advantage in using a small light bomb arises from the fact that the lag is thus reduced; further, a low total water factor may thus be obtained, thereby reducing the precision necessary in the temperature measurement. However, the water value must not be too small, or the cooling correction will be excessive and its determination subject to rather large error. Another point deserving consideration in this connection is that if a bomb of extremely light weight and consequently low capacity is used, high pressures must be employed in order to insure complete

^a Yearbook for 1915, Am. Soc. Test. Mat., 1916, p. 618.

^b Parr, S. W., An acid-resisting alloy to replace platinum in the construction of a bomb calorimeter: Jour. Am. Chem. Soc., vol. 37, November, 1915, pp. 2515-2522.

combustion of the charge. These will, of course, shorten the life of the bomb.

The wearing parts of the bomb should be heavily built to resist wear, and facility of manipulation should also be considered. The sealing mechanism of the bombs used by the bureau, and subsequently described, was designed by O. P. Hood, chief mechanical engineer of the Bureau of Mines, with both objects in view.

WATER JACKET.

The design of the calorimeter requires considerable attention to assure best results. As is true of the bomb, material as light as possible should be used, but on the other hand the construction must be durable enough to withstand the rough service of continuous routine work; and it is of prime importance that material of medium conductivity be used in the heat-absorbing parts. The effect of lag introduced by small weights of substances of low conductivity is obviously to render the inflection points of the time-temperature curve less sharply defined, thus leading to uncertainty in the cooling correction.

It is now generally recognized that a stirred water jacket is necessary and that temperature control is highly desirable. A complete water jacket, although not absolutely essential, will minimize the effect of variations in room temperature, and if the calorimeter is provided with a water seal, that part of the heat transfer equation

$\theta = \theta_0(1 - e^{-kt}) + \int_0^t f(t)dt$ which has to do with the correction factor

$\theta_0(1 - e^{-kt})$ may be definitely known and controlled. Thus greater accuracy and rapidity are insured, for if the cooling constant of a calorimeter is known, there is no need of making the preliminary and final rate observations, and the time required for a determination is therefore considerably shortened. With the design calling for the use of the Dewar cylinder in lieu of a jacket, the assumption is made of course that the cooling correction either does not enter at all, or is reduced to a negligible minimum. However, the authors' experience with the average Dewar flask would indicate that there would be an appreciable heat exchange in the system. Moreover, this type of apparatus, as compared with the water jacket type, would not seem to offer greater accuracy or convenience.

STIRRER.

Efficient stirring of the calorimeter liquid is important. The rate of stirring must not be too fast, as such stirring produces an excessive amount of heat—the exact amount being hard to control and to determine—nor must it be too slow, for that leads to inefficient mixing.

There is no exact criterion for determining the proper rate; however, the statement is made by Committee E-4 of the American Society for Testing Materials^a that the heat input from the stirrer should not exceed 0.01° C. per minute for the average water-equivalent value of the bomb.

The turbine stirrer is, all things considered, best adapted to the closed calorimeter and is easiest to control. The speed at which the stirrer runs may be not over 500 revolutions per minute and still give efficient mixing, if the stirrer itself is well designed. The diameter of the blade wheel should not be less than $1\frac{1}{4}$ inches, and in many installations can be increased to 2 inches, reduction in speed being necessary. In the turbine stirrers with which commercial calorimeters are usually equipped, the propeller blades are not carefully designed and an excessively rapid rate is necessary to insure the necessary mixing. The blades should receive as careful thought as the propellers of a boat, as the same principle of energy distribution is involved. The object is obviously to move the greatest amount of water for a given speed, with the least slip, and, consequently, with minimum heat input.

THERMOMETER.

Temperature-measuring devices should receive careful attention. Next to such obvious requirements as constancy, uniformity of scale, and small lag, perhaps the most desirable features are high sensibility, facility of checking the fundamental interval, and ease of reading and manipulation.

ADVANTAGES AND DISADVANTAGES OF MERCURY THERMOMETER.

The mercury thermometer possesses the advantages that it is simple, inexpensive, and fairly constant. However, it has, unavoidably, considerable lag; instruments of uniform bore are difficult to obtain and the highest sensibility obtainable therewith leaves much to be desired. It is impossible to determine the fundamental interval for thermometers adapted to calorimetry; and, further, the mercury thermometer possesses the unique disadvantage that the mercury often sticks in the bore, thus rendering the readings uncertain. This last trouble can be alleviated, but not entirely cured, by the use of an electric tapping device. A miniature electric buzzer held fixed in contact with the thermometer stem and operated through a button conveniently placed is the form of device usually employed. Even when the thermometer is thus tapped, the mercury column may not always reach equilibrium, particularly in thermometers with small bulbs and small bores.

^a Yearbook for 1915, 1916, p. 618.

GRADUATION.

The thermometer should, by all means, have scale divisions extending fully down to the bulb. The Beckman thermometer, in particular, is often constructed with a considerable length of stem between the bulb and the scale. The volume of the bore for this space can not be well determined; in fact, it is usually considerably larger than that of the capillary under the scale divisions, and, consequently, the application of a stem correction is impossible.

CALIBRATION.

As to the calibration of calorimetric mercury thermometers—the certificates of calibration usually furnished with such instruments give corrections only at whole-degree or, at best, half-degree intervals, leaving considerable uncertainty as to just how the bore varies between the intervals. An examination of the table of corrections given below for a direct-reading Golaz thermometer, in which the bore is rather better than the average, will make this point clear.

Table of corrections, Golaz mercurial thermometer.

Thermometer reading, ° C.	Correction, ° C.	Thermometer reading, ° C.	Correction, ° C.
18-----	0.000	24-----	—0.032
19-----	.000	25-----	— .028
20-----	— .010	26-----	— .022
21-----	— .020	27-----	— .026
22-----	— .022	28-----	— .032
23-----	— .028	29-----	— .040

The assumption is made, of course, that the variation is proportionate to the scale divisions between intervals, but the assumption may prove only approximately correct. One would hardly expect to obtain readings correct to 0.001° C. when such an uncertainty exists. Obviously, it is advisable to determine the bore variations by the well-known broken-thread method, if it is desired to get the best results of which the mercury thermometer is capable.

The authors prefer a relatively large bore, direct-reading thermometer with solid-glass stem, and having scale divisions at intervals of 0.02° C. Divisions at 0.01° intervals are, of course, an advantage, but when the reading is done with a high-power cathetometer, this refinement is not essential.

Should higher sensibility and greater accuracy than that of which the mercury thermometer is capable be desired, two electric methods—the resistance and the thermoelectric—are available. It is possible with the resistance method to obtain an ultimate sensibility of 0.0001° C., well-constructed platinum resistance thermometers and appropriate measuring devices being used; also, the apparatus is well adapted for close calibration. The equipment is rather more ex-

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pensive than that required for the thermoelectric method, but on the whole is perhaps better adapted to the usual form of combustion calorimeter.^a

The thermoelectric method^b has the advantage that apparatus suitable for a given sensibility is considerably less expensive than that required with the resistance method; in fact, the ultimate sensibility obtainable is considerably in excess of that obtainable with the resistance method. Further, the thermoelectric method is well adapted to the reading of a number of temperatures in rotation. With the resistance method, such reading is troublesome and requires expensive apparatus. However, the resistance method of reading temperatures in a single combustion calorimeter is perhaps the simplest.

APPARATUS USED BY THE BUREAU OF MINES.

The objects kept in view in the design of the bureau's calorimeters were: Facility of operation, compactness, durability, and a higher accuracy than that of the usual commercial calorimeter. As 90 to 150 determinations had to be made daily, it was necessary to consider the maximum capacity with a generous allowance for accidents, rush samples, etc. Compactness was obtained by mounting all the calorimeters on one framework and the time required for a determination was considerably shortened through the application of the complete water jacket and the constant-temperature bath. A tank was also provided for supplying water to be used in the calorimeters, and the temperature of the water in the tank was controlled by a thermostat, the usual inconvenience of adjusting the temperature of the water previous to each determination being thus avoided. The water is measured by an automatic overflow pipette. When the inlet cock is opened, the pipette fills and overflows through a small outlet at the top. When the water is needed, the intake cock is closed, the outlet is opened, and the water is drawn off to a graduated point on the pipette. As the water is always measured at the same temperature, this measuring can be done accurately and conveniently and the time required for measuring is considerably less than would be required for weighing. A change-over mercury contact controller or distributor switch for the thermometers, carrying also ordinary brass contacts for the firing and heating circuits, was constructed so that by one operation the operator can shift all electric circuits from one calorimeter to another. This switch is described in detail on page 24.

^a Dickinson, H. C., and Mueller, E. F., New calorimetric resistance thermometers: Bull., Bureau of Standards, vol. 9, October, 1913, pp. 483-492.

^b White, W. P., Thermoelement installations, especially for calorimetry: Jour. Am. Chem. Soc., vol. 36, September, 1914, pp. 1856-1868.

THE BOMB.

The bomb (Pl. I and fig. 1) consists of a gold-plated, cylindrical, monel-metal shell of about 600 c. c. capacity. The sealing device consists of a tough steel receiving nut and lock, so constructed that

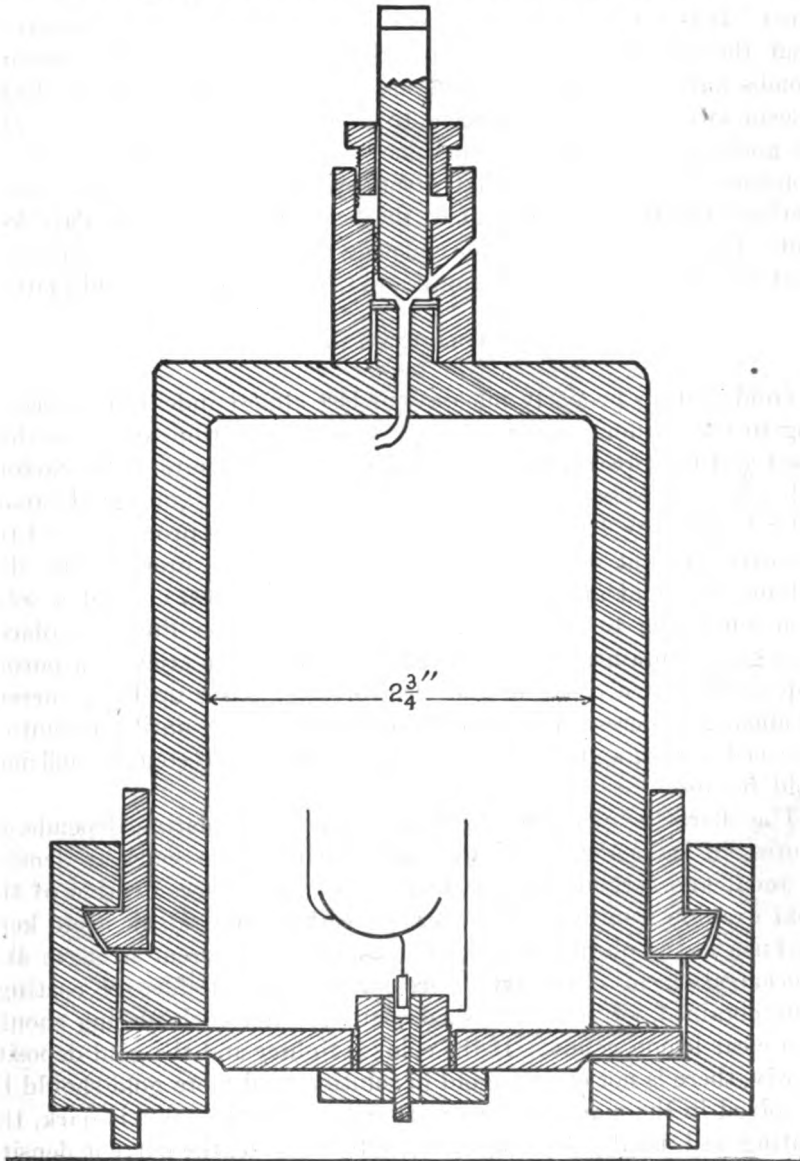


FIGURE 1.—Vertical cross section of bomb.

less than a one-eighth turn with the wrench suffices for sealing. A circular gasket of electricians' solder effects the seal. This locking device, which was designed by O. P. Hood, chief mechanical en-

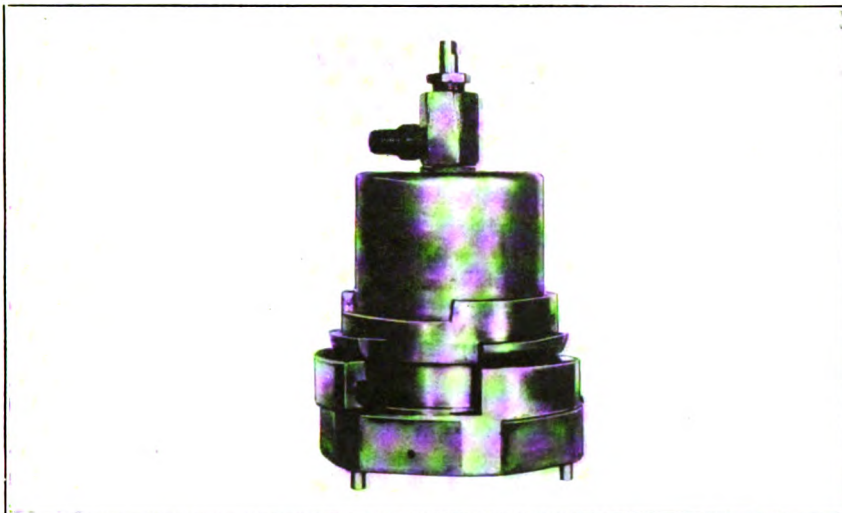
gineer of the bureau, is an adaptation of the principal used in breech locks of cannon. The advantageous features of the design are briefly: Durability, ample strength, and facility of manipulation. Further, when after long service the lock wears out, a new lock can be substituted without the expense of making and plating a new shell. It is noteworthy, so far as this last desideratum is concerned, that the designer builded better than he thought. The bureau's bombs have been in continuous use for three years, and the locks, except two that were subjected to excessive strain, are practically as good as new. In the experience of the authors, this service is considerably better than that given by any threaded bomb, except perhaps the Parr, on account of the heavy threads of the Parr lock nut. The principal reason for choosing monel metal for the shell was that the metal has ample strength and is well adapted to gold plating.

GOLD PLATING.

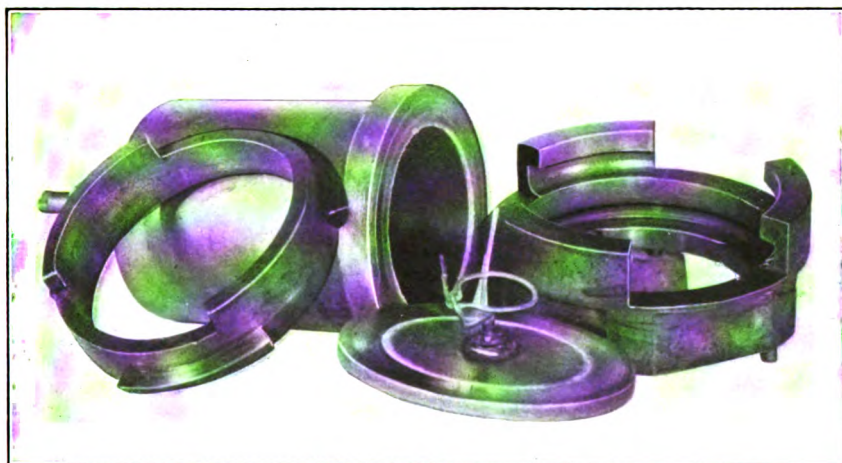
Gold plating properly put on will last almost indefinitely according to the author's experience. A brief description of the method used and the precautions observed in order to insure a satisfactory job will perhaps be of interest here. First, a slab of pure gold (about 2 by 4 inches by $\frac{1}{8}$ inch) to serve as an anode was procured, and the required amount of gold potassium cyanide was prepared by dissolving the gold anode electrolytically. About 600 c. c. of a solution containing 40 grams of potassium cyanide per liter was placed in a glass container with the gold anode, a carbon stick in a porous cup serving as a cathode, and electrolysis was set up by a current of about 2 amperes. The electrolysis was continued until the solution attained a dark-amber tint, when it was judged to contain sufficient gold for use.

The character of the gold deposit obtained in plating depends, of course, in large degree on the plating conditions—current density at anode and cathode surface, temperature, and concentration of the gold cyanide solution. The areas of cathode and anode were kept uniform in the plating of these bombs, and the current strength and concentration of electrolyte were varied till satisfactory coatings were obtained. The unburnished coatings after each plating should be a clear lemon yellow. If the color is lighter and the gold deposits slowly, there is not enough gold in solution, and more gold should be dissolved in the manner already described. If the color is dark, the plating will usually show a tendency to crumble, the current density having been too high. This fault can be corrected by lowering the current density and diluting the electrolyte.

The best conditions for the plating job at hand having been learned by trial, it will usually suffice in applying subsequent coatings to keep the current density constant, a little potassium cyanide being added



A. BOMB, ASSEMBLED.



B. DETAILS OF BOMB.

from time to time when the rate of deposition becomes slow and the color of the coating becomes too light.

The preparation of the surfaces for plating requires extreme care. The surfaces must, of course, be machined smooth (and it is preferable that they be polished) and be free from all adherent foreign matter. Grease is the worst enemy of the plater; the slightest trace of it on the surface results in the peeling off of the deposited gold. The Bureau of Mines bombs were first immersed for about 15 minutes in a boiling solution of a strong caustic, subsequently washed with ether to insure the removal of every trace of grease, then washed with distilled water, and then they were ready for the plating bath.

The plating apparatus consisted of a spindle, to which the anode could be attached, connected through suitable driving gear to an ordinary fan motor, by which it could be rotated at the rate of 60 to 80 revolutions per minute; a heated water bath for keeping the gold solution near the boiling point; and suitable clamps for attaching the electrical lead wires to the rotating anode and bomb. The cleaned bomb was placed in the water bath, the electrical connections made, and the water in the bath heated to boiling. The hot cyanide solution was then poured into the bomb, the anode set in rotation, and a current of about 1.5 amperes passed through the solution. This current strength was about right for the 600-cubic-centimeter bomb and the anode surface above specified.

The first deposition was allowed to go on for 15 minutes, when about 2 grams of gold had been deposited. The bomb was then removed from the bath, the solution poured out, and the bomb washed free from cyanide. The plating was then scratch burnished until bright by a brass-wheel brush mounted on the spindle of a polishing motor, all loose gold being removed. A burnishing liquid was made by boiling flaxseed meal with water, and with this liquid the surface of the plating was kept moist during the burnishing, in order to prevent undue tearing of the gold. The bomb was then again boiled with caustic and another 15-minute coating was put on. This coating, provided there had been no peeling off of the previous coat, was burnished with a jeweler's agate burnishing tool. The bomb was mounted on the spindle of a low-speed motor and rotated, while the agate tool was held on the surface to be burnished until it became uniformly bright. If the first coating came off in patches, owing to the presence of grease, the scratch burnishing was continued with succeeding coats, care being taken with the washing, until a perfectly adherent film was obtained.

About 15 coats were then put on, each coat being burnished with the agate tool and the burnishing liquid being freely used with each burnishing. A total of about 2 ounces of gold was used in plating the bomb. The surface was then tested by allowing it to remain for

about two hours in contact with hot concentrated nitric acid. In every case the acid solution after the test showed no trace of copper or nickel. The plating was accordingly assumed to be acid proof and three years' use of the bombs has justified that assumption.

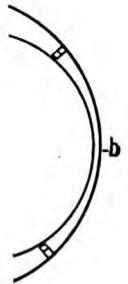
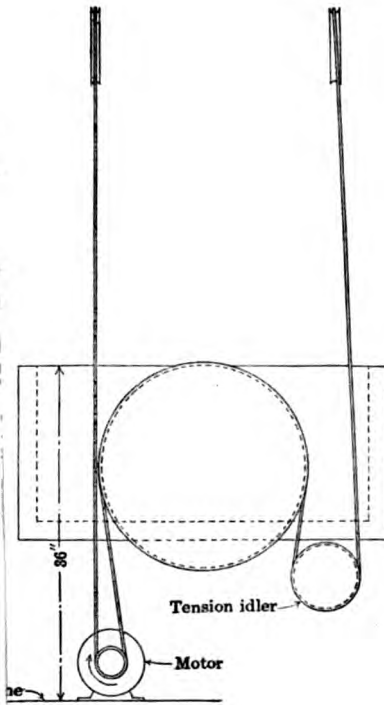
The bottom plates of the bombs, which carry the insulated ignition electrode (see fig. 1), were plated in the same manner, except that a bath of an appropriate size was used and also a smaller anode. The oxygen intake was made of a gold tube so expanded into the intake opening as to be acid-proof. The valve used on the bomb is the ordinary needle valve seated in a hard-rubber washer or gasket. The method of supporting the charge is shown in fig. 1. The supporting electrodes were of platinum wire, 2 millimeters in diameter.

CALORIMETER CAN.

The calorimeter, shown in some detail in figure 2, consists of a cylindrical can made of heavy sheet brass, reinforced at the top and middle with brass bands $\frac{1}{2}$ inch by $\frac{3}{4}$ inch. (See A, fig. 2.) A tubular stirrer well is soldered to the can, as shown in B. Suitable brass guides are soldered to the inner surface of the can in such a manner as to insure uniform plating of the bomb for every determination. An electrode, consisting of a $\frac{1}{8}$ -inch brass bolt provided with a stiff brass spring for contact with the bomb plug, is let through a hole in the center of the can bottom and is insulated from the metal of the can by means of a sleeve and washers of hard rubber. The electrode and a similar device on the jacket can serve to establish an insulated electrical path from outside the apparatus to the fuse holder inside the bomb. The can is supported in the jacket by small studs of ivory mounted in conical brass tubes and soldered to the bottom and surface of the jacket can. (See A, fig. 2.) The studs have a minimum contact surface and serve as guides for the calorimeter which must occupy the same relative position in the jacket can at every determination. The jacket can is cylindrical, is made of heavy sheet brass, and is provided with a cover of brass ground to a water-tight fit. The cover is provided with a thin sheet-brass water seal (fig. 2) fixed to the cover proper by means of three thin insulating rods of ivory in such a manner that when the calorimeter is in place and the cover brought down snugly the water seal is in contact with the surface of the water in the calorimeter can, thus serving as an effectual seal against evaporation into the space between the calorimeter and the jacket can. The importance of an effective water seal is shown below.

Soldered to the jacket can are two heavy brass lugs, by which the jacket can is held to the vertical brass T bar of the frame in such a manner as to permit the can to slide vertically. The can is supported at the bottom by a heavy helical brass spring bearing against the bottom of the tank (A, fig. 2), and of such strength that the can when

TECHNICAL PAPER 91 PLATE II



through ab,
de, showing

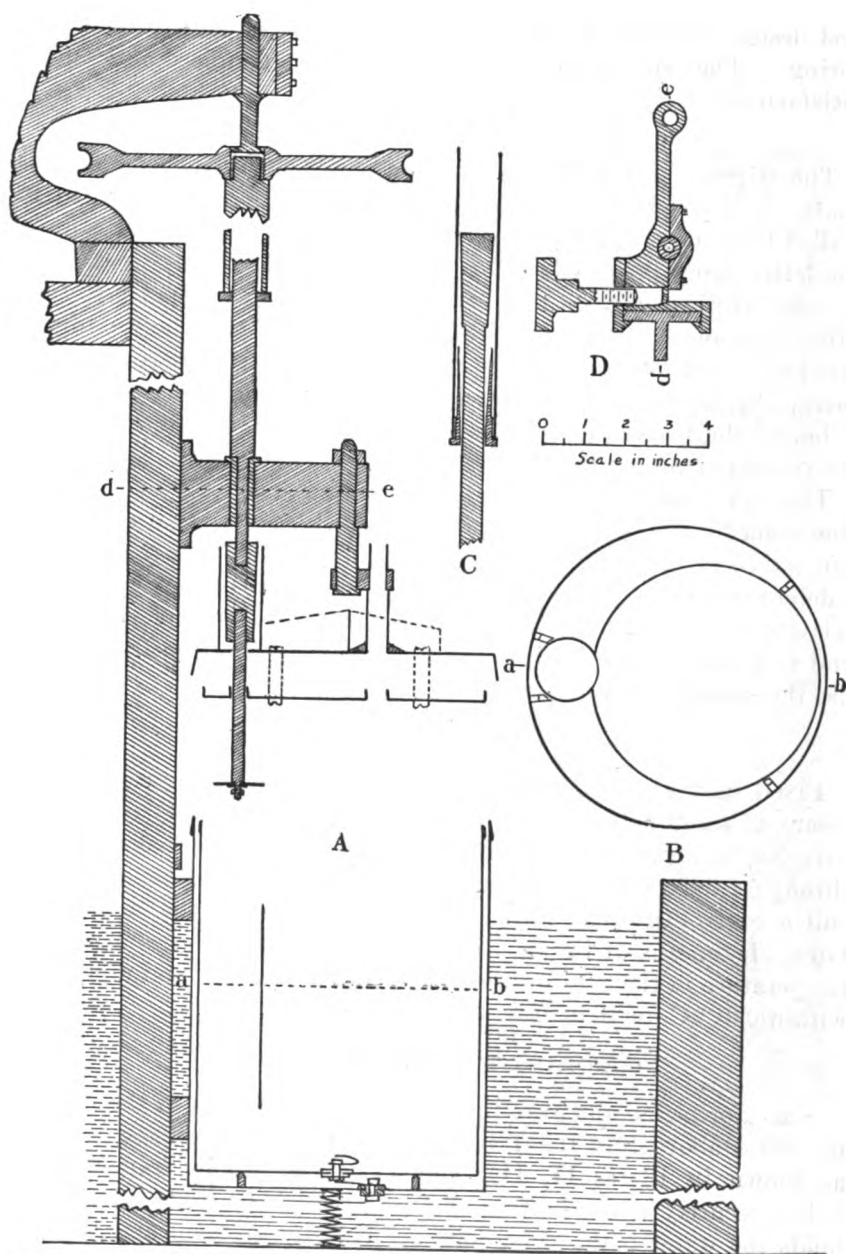


FIGURE 2.—Details of calorimeter. A, vertical section; B, horizontal section through ab, showing tubular stirrer well; C, shaft clutch; D, horizontal section through de, showing lid bracket.

charged is held vertical, with its top slightly above the surface of the tank water, against an adjustable stop fixed to the **T** bar. In the first design, shown in Plate II, a counterpoise was used instead of a spring. The spring, however, was found simpler and more satisfactory.

STIRRER.

The stirrer shaft is shown in figure 2. The upper part of the shaft, on which the driving wheel is mounted, consists of a thick-walled brass tube, into which the lower part of the shaft telescopes, the latter being provided with a conical piece (C, fig. 2) screwed to the end which engages a receiver at the lower end of the shaft tube after the manner of a conical friction clutch when the whole calorimeter is lowered into place. The lower bearing of the stirrer shaft is carried by the lid bracket (D, fig. 2), which is held to the vertical **T** bar of the frame by a clamp which permits raising and lowering the lid and clamping in any desired position.

The calorimeter cover has tubular outlets (not shown) for the thermometer, the stirrer shaft, and electrical leads, so that the jacket can and cover may be totally immersed in the water of the tank during a determination. The position of the propeller stirrer is always fixed relative to the jacket can lid, so that when the calorimeter is charged and in place and the lid brought down the stirrer propeller always has the same position in the stirrer well.

LEAD WIRES.

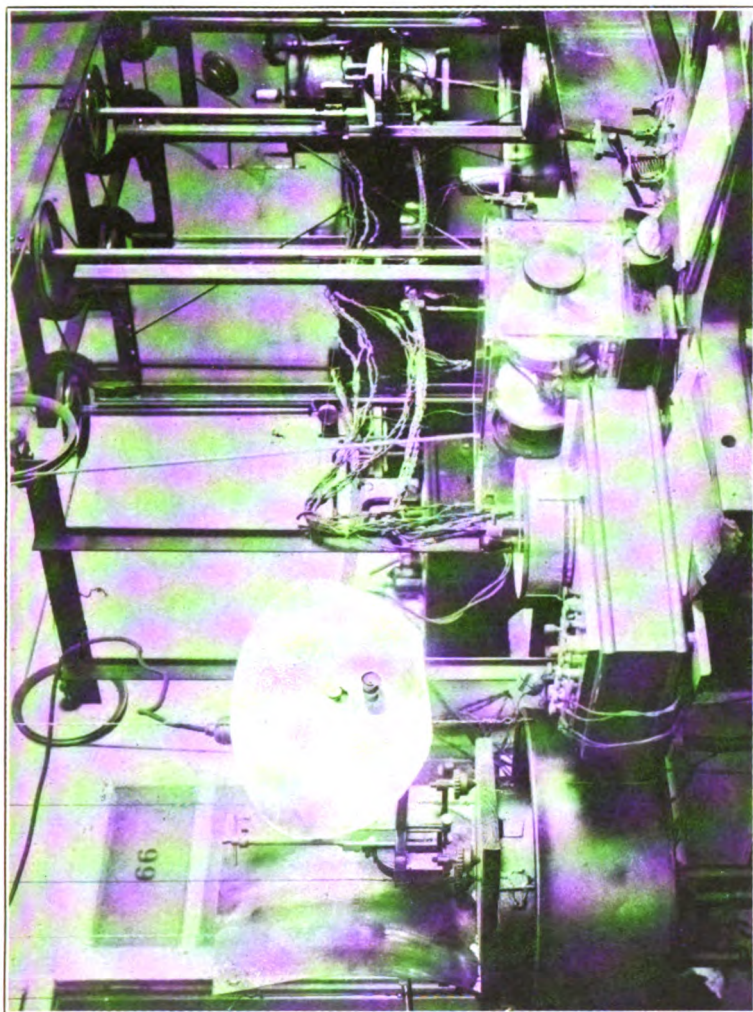
Fixed to the calorimeter water-seal and insulated therefrom by means of small rubber disks, is a resistance coil (about 5 ohms) of bare No. 22 nichrome wire which is connected by suitable leads and through a fixed external resistance to the lighting mains. This circuit is controlled by a switch conveniently placed on the observation table. By means of the device, before a determination is made, the temperature in the calorimeter can be adjusted easily and quickly to within 0.01° C. of that desired.

CONSTANT-TEMPERATURE BATH.

Six calorimeter units are mounted on brass **T** bars in the manner described above, and the **T** bars are bolted to heavy brass castings as shown in Plates II, III, and IV. The whole framework is bolted securely to the bottom of a heavy alberene stone tank which holds the water bath. The bolts are held by glycerin and litharge cement. The tank (Pl. II) is built of stone slabs, those used for the sides of the tank being $1\frac{3}{4}$ inches thick and those for the bottom 2 inches thick. They are 8 feet long, 3 feet wide, and 17 inches deep. The tank is supported by a framework of $2\frac{1}{2}$ -inch black-iron pipe, put together by means of suitable cast fittings. A waste valve and an

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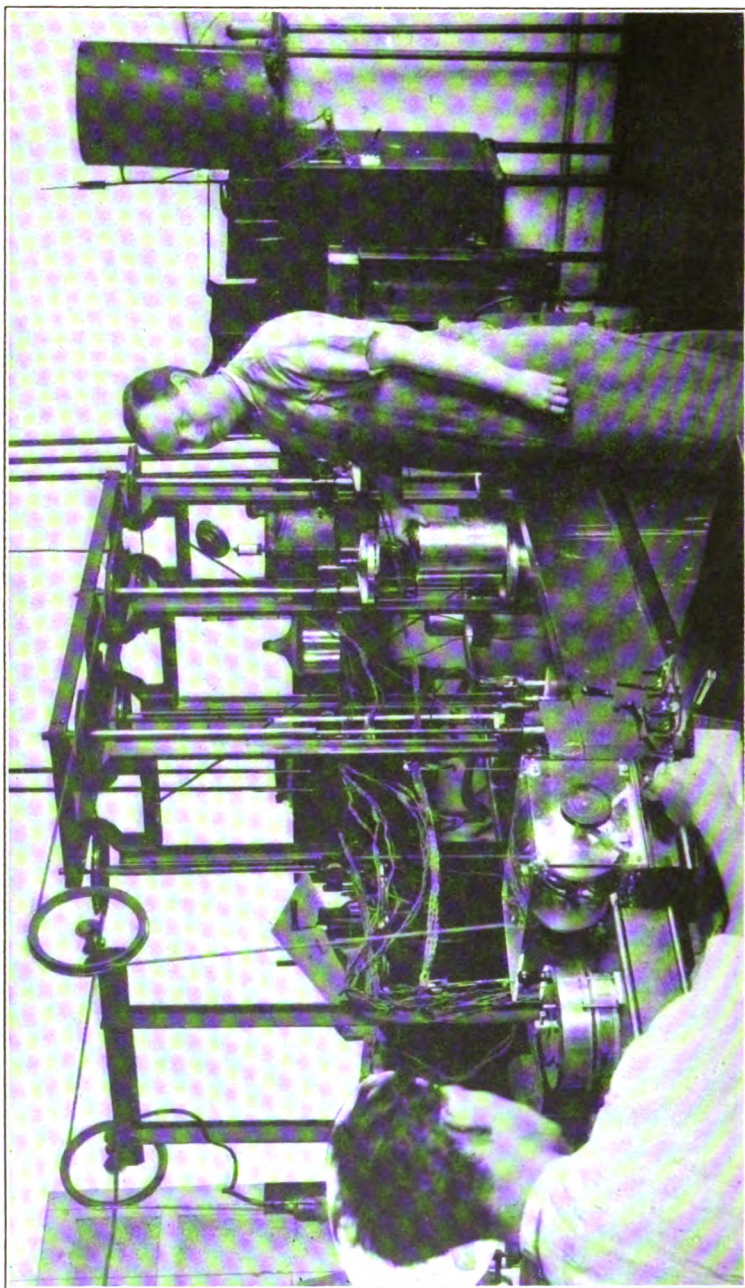
TECHNICAL PAPER 91 PLATE III



GENERAL VIEW OF CALORIMETER EQUIPMENT.

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TECHNICAL PAPER 91 PLATE IV



ANOTHER VIEW OF CALORIMETER EQUIPMENT.

overflow pipe are provided for the tank and are connected directly with the laboratory waste system. Through the center of the tank is mounted a $9\frac{1}{2}$ -inch seamless brass tube (Pl. II), securely bolted to the calorimeter-support framework. In the end of this tube, the stirrer is mounted. The stirrer consists of a small motor-boat propeller, mounted on a brass shaft and held by a water-tight boxing, bolted through the tank and driven by means of the pulley shown in Plate II. The pulley is a 24-inch bicycle wheel and is bolted securely to the stirrer shaft.

The speed of the stirrer is about 200 revolutions per minute, and it effects mixing by pumping the water from one end of the tank to the other, the current being always in the same direction relative to the calorimeter units. A $\frac{1}{2}$ -horsepower motor is used for driving the tank stirrer and the stirrers for the individual calorimeters, transmission being effected by an endless belt, about 50 feet of $\frac{1}{4}$ -inch cotton sash cord. The speed of the calorimeter stirrers is 750 revolutions per minute, and because of the excess power of a motor running at practically constant voltage this speed is constant within narrow limits.

TEMPERATURE CONTROL OF THE BATH.

The temperature of the tank is kept at $30^{\circ}\text{C. } (\pm 0.02^{\circ}\text{C.})$, and as the room temperature is usually lower means must be provided for supplying heat to the tank. The heat necessary is mostly supplied by hot water which is allowed to flow into the tank, the amount supplied being dependent on the temperature difference, the residual small amount of heat necessary being put in by means of twelve 120-watt carbon filament incandescent lights, set into the tank walls and controlled by means of a sensitive thermostat. The thermostat consists of a sealed thin brass tube about 20 inches long and $1\frac{1}{4}$ inches in diameter, filled with toluene and provided with a flexible copper tube of $\frac{1}{8}$ -inch bore for outlet. The open end of the copper tube is soldered to the platinized-glass end of the regulator tube as shown in figure 3.

The joint between the brass and the copper tubing is a nut through which the copper tube is passed and soldered in position. A lead gasket, fitted on the nut shoulder, serves to make the joint perfectly tight. Two thin platinum wires are sealed into the U tube of the regulator *b* (fig. 3) at the points indicated and are connected through a 250-ohm relay, *d*, to the battery *e*. The U tube of the regulator is of about 1 mm. bore and is filled with mercury to the level indicated.

The lower wire is always in contact with the mercury, but the wire above makes connection only when the tank water is being cooled, and, consequently, the toluene is contracting. The mercury

then rises in the tube, closes the circuit through the relay *d*, which closes the circuit connected with the lights inside the tank. The temperature of the tank water then rises, the thermostat liquid expands, and the circuit through *d* is broken. The thermostat, thus used, constantly opposes radiation from the tank water. It may be used also to oppose heat absorption by the tank. For this purpose the relay *e* is provided connected in series with a platinum-wire contact in the open end of the regulator tube and to the battery *c*. This relay controls the magnetic lift valve *f* on the ice-water tank *g*. As will be seen, when the thermostat expands, the relay *e* operates the magnet *f* and lets ice water into the tank, thus effecting temperature control.

When the calorimeter outfit was first installed, all calibrations were made with the thermostat set at 26° C. Later during hot

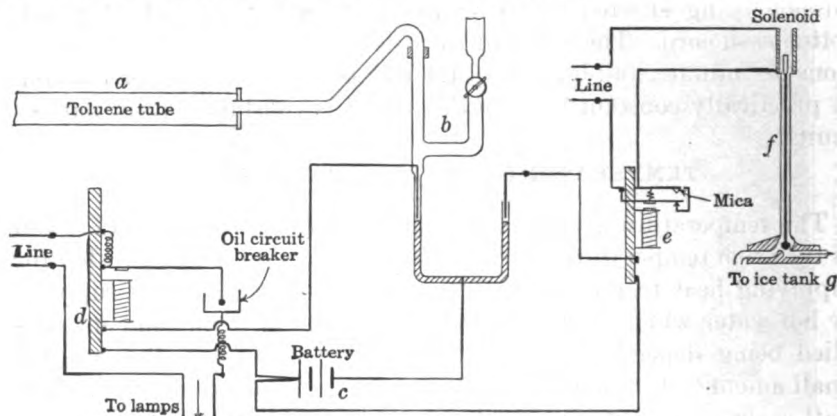


FIG. 3.—Device for regulating temperature in tank.

summer weather operation at so low a temperature proved impracticable, as through the deposition of moisture on the calorimeter the calorimeter temperature was often below the dew point. The working temperature of the tank water was therefore made 30° C.

The brass tube or bulb of the thermostat is supported horizontally within the stirrer tube of the tank. It was at first anticipated that the thermostat would be subject to such excessive lag as to reduce greatly the available sensibility, and two auxiliary lamps connected to the controlled circuit were so mounted that their position relative to that of the thermostat bulb could be changed at will. The effect of these auxiliary lights was to boost the thermostat, as it were, at the time when the heating circuit was first closed. The boosting effect could be obtained on the cooling side by directing the incoming stream of cold water onto the bulb. Although it was evident that the auxiliary lights made more accurate temperature control possible, it was found that the control was satisfactory without their use, and they were discarded.

DEVICE FOR HANDLING WATER FOR THE CALORIMETER.

TEMPERATURE CONTROL.

The usual method of adjusting the temperature of water for the calorimeter by mixing it in a flask with ice water and subsequently weighing or measuring a given volume from the flask is somewhat inconvenient. To obviate this difficulty, the authors have provided a stone tank or reservoir, built to hold about 20 gallons of water and provided with a thermostat for accurate temperature control. As the water from previous calorimeter determinations is turned back into the tank, the thermostat must cause the temperature to be lowered. This is done by ice water kept in a tank at a higher level than the reservoir tank and let into the lower tank by a valve operated by a magnet in the thermostat circuit. The valve is similar to that used with the calorimeter thermostat and functions in the same manner. The thermostat bulb, however, is different, being made of glass and having mercury as the sensitive element. The construction of the bulb is shown in figure 4.

The bulb *a* for the mercury is about 20 cm. long and has a 12-mm. bore. The end of the tube is drawn out, and the side tube *b* carrying a stopcock is sealed on. To the vertical branch is sealed the capillary tube *c*, of about 0.8-mm. bore. Electrode *e* is sealed into the side branch *b*, as shown, and a thin, pointed wire, *d*, which may be inserted into the capillary to any point, serves as the other electrode. To set the thermostat, the cock is left open while the temperature of the tank water is brought to the desired point; the electrode *d* is then brought to that point, the cock closed, and the electrical connections made. The tank water is stirred continuously by a 4-inch propeller, driven by a small fan motor. The temperature of the water may thus be kept constant to 0.1° C. without further attention, other than to occasionally see that the ice-water tank contains sufficient cold water.

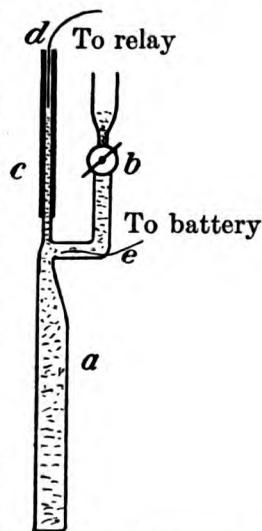


FIGURE 4.—Thermostat for temperature control of calorimeter water.

MEASUREMENT OF WATER.

The water for the calorimeters is measured by means of a large automatic pipette, provided with an overflow pipe and glass stop-

cocks, and as the water measured is always at the same temperature, one calibration point is all that is needed, and the water is delivered directly into the calorimeter pail.

TEMPERATURE MEASURING DEVICE.

Temperatures within the calorimeters are measured with platinum resistance thermometers, having a sensibility of about 0.0005°C . and calibrated to 0.001°C . Each outfit consists of a thermometer bulb, a suitable bridge, and a galvanometer for measuring resistances. Three of the thermometers with which the bureau's calorimeters are provided are connected to a special switch of low contact resistance, in order to permit the three instruments being read with one measuring outfit.

The thermometer, which is of the four-lead type and of a design almost identical with that of Dr. E. F. Mueller, of the Bureau of Standards, is shown in figure 5. The sensitive element consists of a coil of 0.1-mm. pure platinum wire, about 1 meter long, wound noninductively on the mica form shown. The resistance of the coil is approximately 25 ohms at 0° , and 35 ohms at 100°C .; or, in other words, the fundamental interval is about 10 ohms. The thermometer has practically

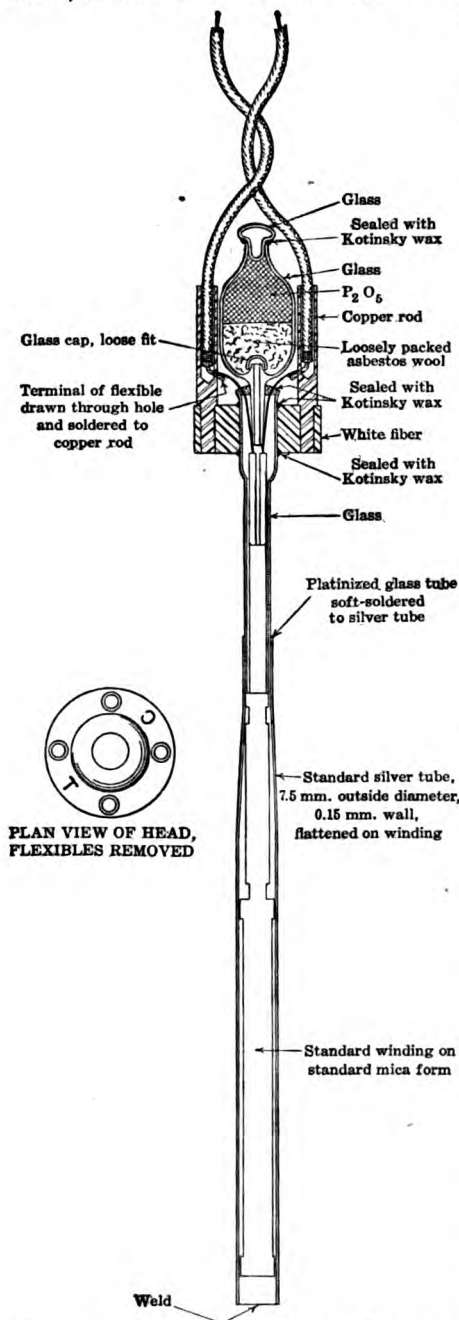


FIGURE 5.—Thermometer used in calorimeter.

no lag and is constant; furthermore, the determination of the fundamental interval presents no difficulties, and the constancy of the in-

strument may thus be verified at any time, if considered desirable. The bureau has used this type of thermometer for the past four years, and during that period has had no difficulty, except that from moisture getting into the thermometer casings, the slightest leak being immediately detected by the "kick" of the galvanometer.

The thermometer casings are made of thin soft material in order that they may be formed over the windings in such a manner that a minimum of air space results, hence they are easily worn through at the edges—the source of trouble with the bureau's instruments. The remedy consists in binding the edges with No. 24 copper wire and soldering the wire to the casing.

Sometimes, after long service, a few strands of the flexible leads may become broken, thus introducing a variable resistance. Broken leads may be detected by placing the thermometer in a bath of constant temperature and moving the leads about with the fingers. If there is a break in the leads the galvanometer, which is at rest in so far as the bridge and the thermometer itself are concerned, will be deflected in an erratic manner. The break may be found by exploring each lead with the fingers, at the same time watching the galvanometer for erratic deflection. A length of bad wire may then be cut out and a new piece soldered in.

REPAIRING LEAKY THERMOMETERS.

When a thermometer develops a leak, the trouble is invariably due to a hole in the metallic casing. When such a leak develops the drying capsule should be opened and the P_2O_5 carefully removed, care being taken that none of the salt gets into the opening leading into the casing. After the capsule has been wiped clean a rubber tube may be attached to the neck, and by applying air pressure while the casing is immersed in water the leak may be readily found. The casing should then be scraped bright and the hole closed with soft solder, a little rosin being used as flux. A salt should never be used as a flux, as some of it may get inside the casing and break down the insulation.

When the casing has been found perfectly tight the thermometer must be thoroughly dried. The drying may best be done by heating slowly to 130° to 160° C. and exhausting the air with a good pump. The last trace of moisture is thus easily and completely removed. Fresh drying salt should be placed in the capsule and it should be sealed with Khotinsky wax. The thermometer is then ready for service. After a thermometer has been repaired it is well to check the figure previously obtained for the fundamental interval in order to make sure that there has been no change in resistance introduced.

THE BRIDGE.

An exceptionally good bridge is required for the calorimeter resistance thermometer. In order to obtain readings correct to 0.001°C . with the thermometer described above, the bridge temperature (even with the best wire) must be kept constant during the measurement to a small fraction of a degree. Obviously, the best way to accomplish this is to provide the bridge with a stirred oil bath, the temperature of which may be kept constant within any desired limit. This method, however, introduces certain complications, particularly in connection with the oil bath. As in calorimetry only differences in temperature are required to be measured, and as the time required

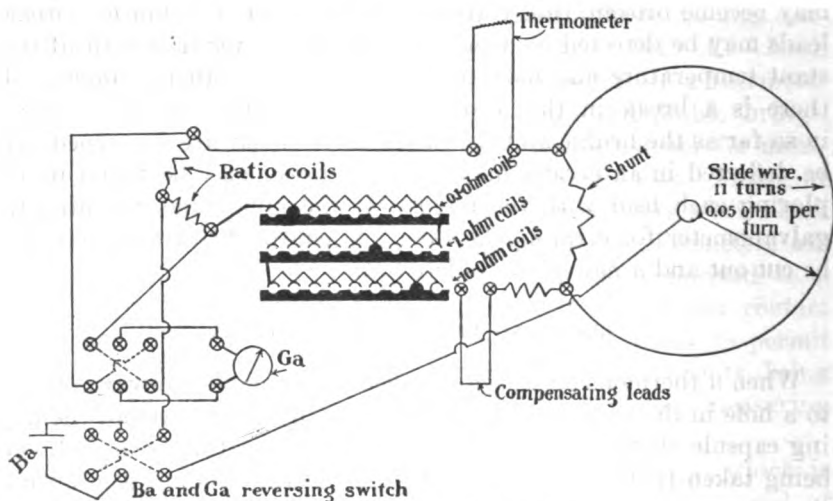


FIGURE 6.—First bridge used.

for a measurement is short, it is necessary merely to guard against sudden and large changes in room temperature, and, accordingly, it is not in general necessary to use the oil bath to obtain the required degree of accuracy. Obviously there must be no appreciable contact resistance introduced during changes of the bridge setting required for a given measurement; such variable resistances must be less than 0.0001 ohm . This requirement would seem to call for all amalgamated switch contacts, which, of course, would mean expensive and cumbersome construction. In order to avoid this the authors some years ago conceived the idea of using a shunted slide wire of sufficient range to take care of the actual calorimetric measurement, the ballast resistance being controlled by switches not to be shifted during the measurement. Dr. E. F. Mueller, of the Bureau of Standards, was asked to design a bridge having the construction indicated, and two instruments were made according to his plans by an instrument com-

pany. Two such bridges have been used with good results by the Bureau of Mines for the past five years. The arrangement of the bridges is shown in figure 6.

BRIDGE FIRST DESIGNED.

The bridge is provided with an adjustable resistance of 100 ohms, in steps of 0.1 ohm, connected in the compensating or measuring arm, the adjustment being effected by means of closely fitting plug contacts. This arrangement gives the bridge a range of approximately 1,000° C. when used with the thermometer described above—a much greater range than is ever needed in combustion calorimetry.

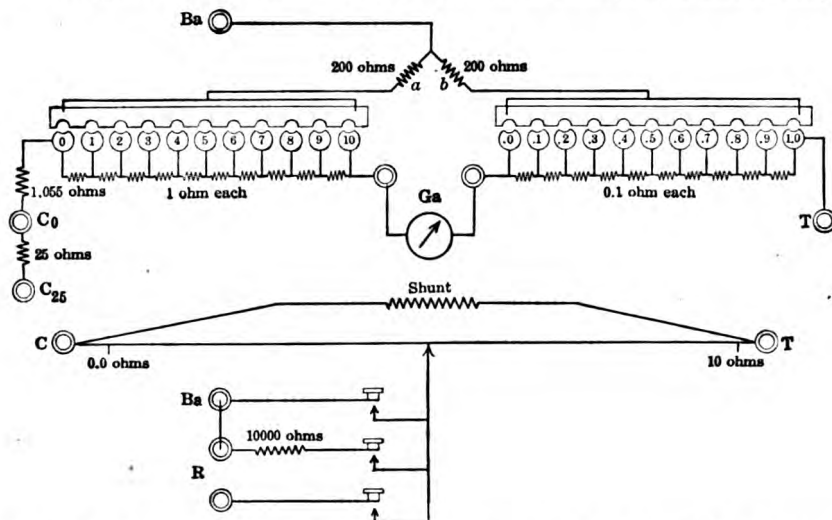


FIGURE 7.—Improved bridge for calorimeter thermometer. Ba, battery; Ga, galvanometer; C, C₀, and C₂₅, compensating leads; T, T, temperature leads; R, resistance.

However, a bridge so constructed may be used for temperature measurement in connection with other work, and with bulbs of different resistances. It is accordingly, of general utility for various purposes than fuel calorimetry.

LATER DESIGN OF BRIDGE.

A special bridge (see fig. 7) designed within the past few years by the Leeds & Northrup Co. embodies the slide-wire principle and is of simplified construction adapted to fuel calorimetry. The range (11 ohms in steps of 0.1 ohm) of this bridge is considerably shorter than that of the one mentioned above, but is sufficient to cover the fundamental interval of a 25-ohm thermometer bulb. Embodied in the design of this bridge are several advantageous features not possessed by the bridge shown in figure 6. A ballast resistance of 25

ohms is provided as shown. This resistance may be inserted in the compensating arm of the bridge, altering the range of the outfit proportionately. Another advantageous feature is the use of three contact keys, one with 0 resistance in series with the battery, one with a resistance of 1,000 ohms, and one left blank for the insertion of any resistance desired. When the resistance of the thermometer is changing rapidly the high-resistance key furnishes a convenient means of following the change approximately without at any time having excessive current going through the galvanometer. As will be noted, the arrangement of the plug contacts is such that the effect of contact resistance is largely neutralized. Except when the fundamental interval is being determined, this feature is, of course, of rather secondary importance, as these contacts are not disturbed during a measurement and should, therefore, have fairly constant resistance.

BATTERIES FOR BRIDGES.

The battery used with the bridges is a No. 6 dry cell, giving a voltage of 1.4, which will cause a current of not over 0.02 ampere to flow in the thermometer. A higher voltage might be employed without damage to the instrument, and in that case, the galvanometer deflections would be proportionately increased. However, excessive current in the thermometer must be avoided, as it results in excessive heating of the thermometer coil, and the readings of the instrument are too high. The lag of the thermometer, of course, is the determining factor; the current should be strong enough to effect the sensitivity desired and should not be so strong as to keep the temperature of the coil appreciably above that of the medium whose temperature is being measured.

THE GALVANOMETER.

A suitable D'Arsonval galvanometer as an indicator to be used with the equipment described will have approximately the following characteristics:

Resistance, ohms	12 to 18
Critical damping resistance, ohms	35
Sensitivity, megohms	190
Sensitivity, m. m. per multivolt	4

Although a short period is desirable, there should be no great sacrifice of sensitiveness to insure it. The best instrument in use in the bureau's laboratories has a period of 45 seconds. In other words, it is advisable to get the best galvanometer obtainable, especially as regards sensitivity. The bridge may be read to 0.00005 ohm, and obviously the galvanometer should be sensitive enough to indicate

a difference of that magnitude. The balance or null method is used exclusively in the bureau's laboratories as being the most convenient, particularly as the range of the bridge is ample, and a telescope and a scale are used to indicate galvanometer deflections.

SUPPORT FOR GALVANOMETER.

Of course, it is necessary to provide the galvanometer with a support that will be free from vibration, and the nature of this support will vary somewhat with conditions in the laboratory. Often a substantial laboratory table or shelf fixed to the wall will prove sufficiently stable. When the whole building vibrates, however, as a result of being situated near heavy traffic, it is necessary to provide some form of support that will absorb vibrations. As the problem differs somewhat with the kind of vibrations to be absorbed, the best form of support to use will have to be determined by experiment. As regards the bureau's apparatus, the support that gave the best results is a modified form of the Julius suspension, which was adopted after numerous other methods had been tried. The suspension consists of a can of sheet brass, *c*, containing a leaden weight, *g*, supporting the galvanometer base, *h*, and suspended at three points from above by iron wires. In the suspending wires are inserted the leaden weight *d* and the coil springs *e*, the strength of the springs, the mass of the weight, and the distance from the galvanometer having been determined by experiment. Further damping was obtained by the oil bath *a*. This consists of a brass can suspended in the position shown by three wires and damped by 2 inches of felt held in light contact with the can bottom by the floor support shown. The galvanometer support can *b* is provided with crossed vanes soldered to its bottom as shown and is adjusted as to height so as to dip into the oil to about the extent shown. The device is not perfect in the sense of damping out all vibrations, but it has greatly reduced them and thus has rendered the effective sensitivity of the galvanometer higher. Obviously, it is useless to attempt to employ a high-sensitivity galvanometer if the vibrations are such as to render its indications uncertain.

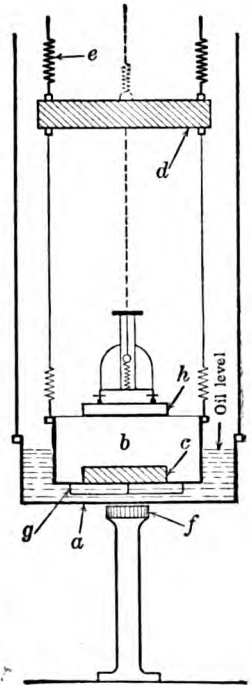


FIGURE 8.—Galvanometer suspension.

DISTRIBUTOR SWITCH.

In order to facilitate the use of one bridge and galvanometer with three calorimeter outfits, a switch (Pls. V and VI) was designed. With this instrument all calorimeter circuits (firing, heating, and thermometer) may be shifted by one operation.

The essential features of the switch are a central cage mounted on the spindle and carrying 16 spring-actuated cooper contact pieces held by hard-rubber bars, the thermometer switch, and two double-pole four-way rotary switches mounted in hard rubber on the same shaft as the thermometer contacts and serving to shift the heating and firing circuits. The master contact pieces of the thermometer circuit are of copper and are bolted securely through the hard-rubber switch base. Terminals are soldered direct to these contacts and connected in the same manner to the bridge terminals. All thermometer contacts are amalgamated to insure minimum contact resistance and the terminal connections are all soldered or welded for the same reason.

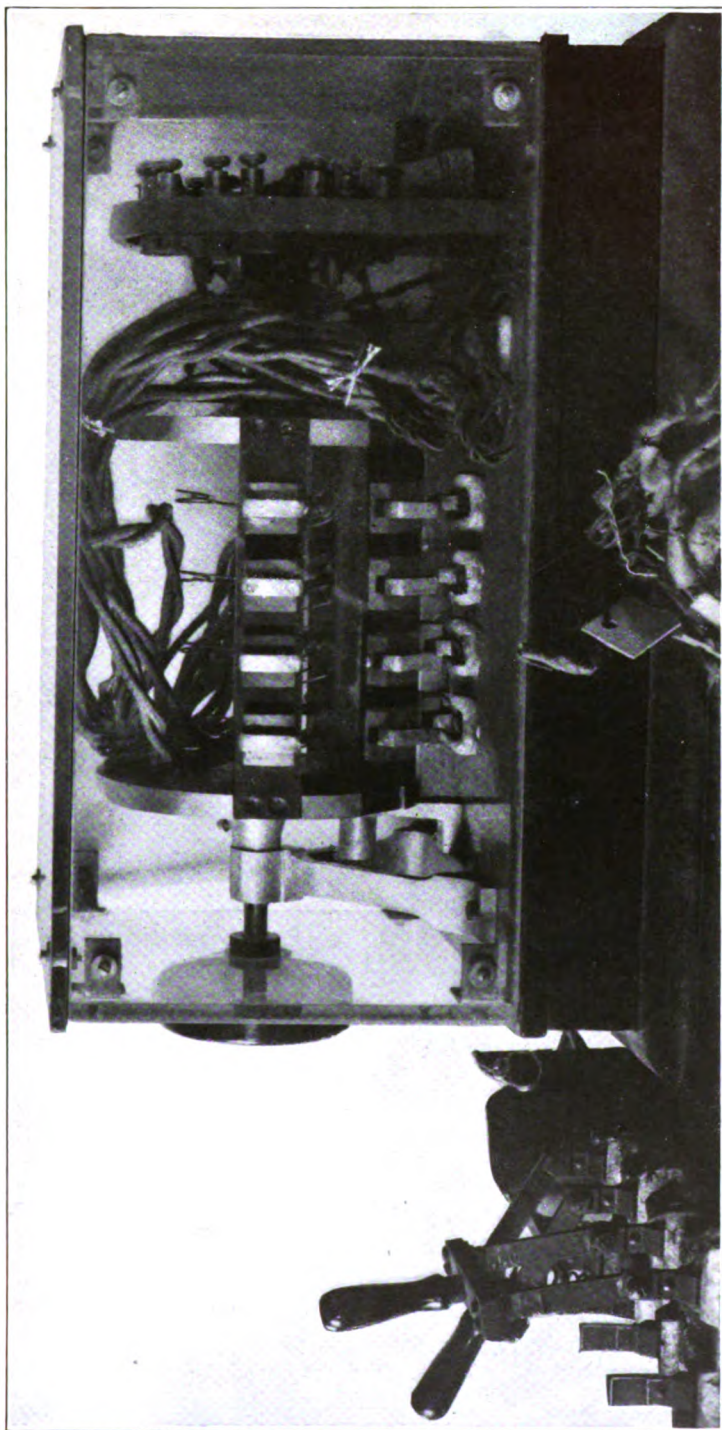
With this switch it is easy to compare closely two thermometers immersed in the same bath; in fact, readings for two thermometers in the same calorimeter can readily be obtained. Further, by using an extra set of contacts, standard resistance may be inserted at any time, or may be connected permanently. Thus the total bridge resistance may be checked as often as desirable. This device may also be used for determining the absolute resistance of the thermometers at fixed points.

CALIBRATION OF THE BRIDGE.

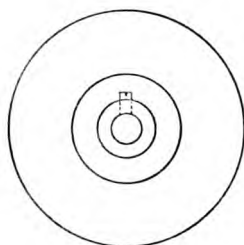
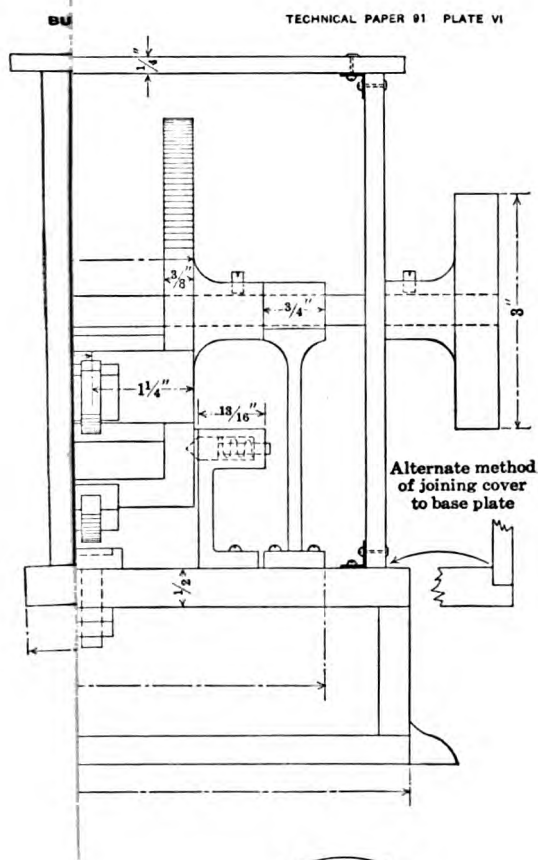
It is absolutely essential that the resistance units of the bridge be accurately determined, and as the determination requires considerable equipment the work had best be done in a properly equipped laboratory. However, the authors have calibrated a bridge by comparison with a similar bridge calibrated by the Bureau of Standards; the results of the comparison are given below.

Results of calibrating coils of Bridge 20300 against coils of Bridge 15749.

Reading, ohms.	[Temperature, about 24° C.]	Corrections, ohms.
3	-----	-0.0021
2	-----	- .0011
1	-----	- .0011
0.9	-----	- .0011
.8	-----	- .0004
.7	-----	- .0003
.6	-----	- .0003
.5	-----	- .0002
.4	-----	- .0001
.3	-----	- .0001
.2	-----	+ .0000
.1	-----	+ .0001



SWITCH FOR USE WITH ONE BRIDGE AND ONE GALVANOMETER WITH THREE CALORIMETER EQUIPMENTS.



SWITCH KNOB

Results of calibrating slide wire of Bridge 20300 against slide wire of Bridge 15749.

COIL OF BRIDGE 15749 SET AT 24.7 OHMS; COIL OF BRIDGE 20300 SET AT 0.2 OHM.

CALIBRATION A.

Bridge 15749.			Bridge 20300.		
Reading.	Corrected reading.	Difference.	Reading.	Difference.	Correc-tion.
0.192	0.191		0.014		
.427	.425	0.234	.248	0.234	0.0
.676	.675	.250	.499	.251	-.1
.976	.974	.299	.800	.301	-.2
1.202	1.199	.225	1.025	.225	.0
1.436	1.434	.235	1.260	.235	.0
1.682	1.681	.247	1.507	.247	.0

CALIBRATION B.

0.197	0.196		0.022		
.432	.430	0.234	.256	0.234	0.0
.681	.679	.249	.507	.251	-.2
.981	.979	.300	.808	.301	-.1
1.207	1.204	.225	1.033	.225	.0
1.442	1.440	.236	1.267	.234	-.2
1.687	1.686	.246	1.513	.246	.0

COIL OF BRIDGE 15749 SET AT 27.8 OHMS; COIL OF BRIDGE 20300 SET AT 3.3 OHMS.

1.633	1.632		1.497		
1.877	1.877	0.245	1.743	0.246	-0.1
2.101	2.101	.224	1.968	.225	-.1
2.335	2.335	.234	2.203	.235	-.1
2.584	2.585	.250	2.454	.251	-.1
2.884	2.885	.300	2.754	.300	.0
3.109	3.110	.225	2.979	.225	.0
3.344	3.343	.233	3.213	.234	-.1
3.627	3.627	.284	3.498	.285	-.1
3.871	3.871	.244	3.743	.245	-.1
4.097	4.096	.225	3.968	.225	.0
4.331	4.329	.233	4.203	.235	-.2
4.580	4.599	.250	4.453	.250	.0
4.877	4.879	.300	4.755	.302	-.2
5.102	5.104	.225	4.979	.224	+ .1
5.337	5.339	.235	5.214	.235	.0
5.608	5.611	.272	5.487	.273	-.1
5.855	5.857	.246	5.734	.247	-.1
6.082	6.082	.225	5.959	.225	.0
6.319	6.317	.235	6.193	.234	+ .1
6.571	6.570	.253	6.446	.253	.0
6.868	6.869	.299	6.747	.301	-.2
7.094	7.095	.226	6.971	.224	+ .2
7.330	7.331	.236	7.206	.235	+ .1
7.605	7.607	.276	7.483	.277	-.1
7.847	7.850	.243	7.728	.245	-.2
8.074	8.077	.227	7.953	.225	+ .2
8.310	8.312	.235	8.188	.235	.0
8.561	8.564	.252	8.440	.252	.0
8.862	8.865	.301	8.742	.302	-.1
9.087	9.088	.223	8.967	.225	-.2
9.323	9.323	.235	9.200	.233	+ .2
9.607	9.608	.285	9.487	.287	-.2
9.849	9.851	.243	9.732	.245	-.2

Results of calibrating slide wire of Bridge 20300 against slide wire of Bridge 15749—Continued.

COIL OF BRIDGE 15749 SET AT 27.8 OHMS; COIL OF BRIDGE 15749 SET AT 3.3 OHMS

Bridge 15749.			Bridge 20300.		
Reading.	Corrected reading.	Difference.	Reading.	Difference.	Correction.
1.636	1.635		1.510		
1.880	1.880	0.245	1.756	0.246	-0.1
2.104	2.104	.224	1.981	.225	-.1
2.337	2.337	.233	2.214	.233	.0
2.588	2.589	.252	2.465	.251	+.1
2.888	2.890	.301	2.766	.301	.0
3.115	3.115	.225	2.993	.227	-.2
3.350	3.349	.234	3.226	.233	+.1
3.632	3.632	.283	3.510	.284	-.1
3.876	3.876	.244	3.755	.245	-.1
4.102	4.101	.225	3.980	.225	.0
4.338	4.336	.235	4.214	.234	+.1
4.588	4.587	.251	4.466	.252	-.1
4.885	4.886	.299	4.767	.301	-.2
5.111	5.113	.227	4.992	.225	+.2
5.344	5.346	.233	5.225	.233	.0
5.615	5.618	.272	5.498	.273	-.1
5.860	5.862	.244	5.742	.244	.0
6.087	6.087	.225	5.966	.224	+.1
6.322	6.320	.233	6.198	.232	+.1
6.570	6.569	.249	6.450	.252	-.3
6.870	6.871	.302	6.749	.299	+.3
7.094	7.095	.224	6.972	.223	+.1
7.328	7.329	.234	7.207	.235	-.1
7.601	7.603	.274	7.483	.276	-.2
7.844	7.847	.244	7.725	.242	+.2
8.070	8.073	.226	7.949	.224	+.2
8.304	8.306	.233	8.183	.234	-.1
8.551	8.554	.248	8.434	.249	-.1
8.852	8.855	.301	8.735	.301	.0
9.077	9.078	.223	8.959	.224	-.1
9.314	9.304	.226	9.184	.225	+.1
9.598	9.599	.295	9.480	.296	-.1
9.842	9.844	.245	9.723	.243	+.2

COIL OF BRIDGE 15749 SET AT 27.8 OHMS; COIL OF BRIDGE 20300 SET AT 3.3 OHMS.

Bridge 15749.			Bridge 20300.		
Reading.	Corrected reading.	Difference.	Reading.	Difference.	Correction.
1.614	1.613		1.464		
1.856	1.856	0.243	1.709	0.245	-0.2
2.080	2.080	.224	1.934	.225	-.1
2.315	2.315	.235	2.169	.235	.0
2.564	2.565	.250	2.418	.249	+.1
2.858	2.860	.295	2.715	.297	-.2
3.083	3.084	.224	2.939	.224	.0
3.320	3.319	.235	3.177	.238	-.3
3.605	3.605	.286	3.464	.287	-.1
3.847	3.847	.242	3.708	.244	-.2
4.073	4.073	.226	3.933	.225	+.1
4.308	4.306	.233	4.167	.234	-.1
4.557	4.556	.250	4.417	.250	.0
4.857	4.858	.302	4.719	.302	.0
5.079	5.081	.223	4.944	.225	-.2
5.315	5.317	.236	5.179	.235	+.1
5.590	5.593	.376	5.455	.276	.0
5.836	5.838	.245	5.701	.246	-.1
6.062	6.063	.225	5.925	.224	+.1
6.298	6.296	.233	6.158	.233	.0
6.547	6.545	.249	6.409	.251	-.2
6.846	6.847	.302	6.710	.301	+.1
7.070	7.071	.224	6.934	.224	.0
7.304	7.305	.234	7.168	.234	.0
7.576	7.578	.273	7.443	.275	-.2
7.820	7.823	.245	7.688	.245	.0
8.045	8.049	.226	7.913	.225	+.1
8.279	8.281	.232	8.145	.232	.0
8.528	8.531	.250	8.396	.254	-.1
8.829	8.832	.301	8.700	.304	-.3
9.055	9.057	.225	8.945	.225	.0
9.290	9.290	.233	9.158	.233	.0
9.575	9.575	.285	9.446	.288	-.3
9.819	9.821	.246	9.692	.246	.0
10.046	10.049	.228	9.921	.229	-.1

Average corrections, slide wire of Bridge 20300.

Reading.	Correction.	Reading.	Correction.	Reading.	Correction.
0-----	0.0	350-----	-.1	700-----	+.1
25-----	0	375-----	-.1	725-----	0
50-----	-.1	400-----	0	750-----	-.1
75-----	-.1	425-----	-.1	775-----	0
100-----	0	450-----	0	800-----	+.1
125-----	+.1	475-----	-.1	825-----	-.1
150-----	0	500-----	+.1	850-----	-.1
175-----	-.1	525-----	0	875-----	-.1
200-----	-.1	550-----	-.1	900-----	-.1
225-----	-.1	575-----	-.1	925-----	0
250-----	-.1	600-----	+.1	950-----	-.2
275-----	0	625-----	0	975-----	-.1
300-----	-.1	650-----	-.1	1000-----	-.1
325-----	-.1	675-----	+.1		

The reader should note that the slide wire is corrected every 25 divisions, and that nowhere does the correction amount to more than 0.2 division, equivalent to about 0.001°C . As this particular bridge is not designed with a range sufficient to cover the fundamental interval, the coils are never used except as ballast, and their accuracy is a matter of secondary importance so long as their resistance is constant. The switches used in the calibration reported above were provided with mercury contacts, short wires of carefully determined resistance soldered to the switch contacts being used to make the adjustments. During the measurements the temperature of all resistances in the measuring circuits was kept nearly constant.

THERMOMETER CALIBRATION.

The bridge calibrated (No. 20300) would not, as it is, serve in calibrating thermometers, as its range is too small. A bridge with 11 to 12 ohms resistance in the measuring circuit and 26 ohms fixed resistance in the compensating arm is required. However, by using standard coils inserted in the compensating arm of the bridge by the mercury-link method, the resistance change covering the fundamental interval might be nearly balanced, and the residual resistance might be taken care of on the bridge slide wire. In this manner, then, this bridge may be used in calibrating thermometers.

Three fixed points on the temperature scale are necessary to establish the relation between differences in temperature and differences in resistance, namely, ice point, steam point, and some intermediate point.

The determination of the ice and steam points^a is effected in the usual way, and the intermediate point may be taken as the transition point of Na_2SO_4 , which is given as 32.384°C .^b

^a Dickinson, H. C., and Osborn, N. S., Specific heat and heat of fusion of ice: Bureau of Standards, Bull. 1, vol. 12, Oct. 28, 1915, p. 49.

^b Dickinson, H. C., and Mueller, E. F., Calorimetric resistance thermometers and the transition temperature of sodium sulphate: Bull., Bureau of Standards, vol. 3, 1907, p. 655.

If the resistance at these points is known, the temperature (H scale) may be calculated by the well-known Callendar formulas, which are as follows:

$$(1) \quad pt = \frac{R_t - R_0}{R_{100} - R_0} 100$$

$$(2) \quad t - pt = S \left(\frac{t}{100} - 1 \right) \frac{t}{100}$$

pt = platinum temperature,

R_t = resistance at the temperature to be determined,

R_0 = ice-point resistance,

R_{100} = steam point resistance,

t = the temperature sought,

and S is a constant depending on the purity of the platinum used.

Its value will be approximately 1.45. The two formulas given above have been shown by Dickinson and Mueller^a to be reducible to the form—

$$(3) \quad R_2 - R_1 = R_0(t_2 - t_1)(a + 2BT)$$

$$a = c \left(1 + \frac{S}{100} \right),$$

$$B = -\frac{CS}{100^2}$$

$$R_{100} - R_0 = R_0(100c)$$

$$\text{and } T = \frac{t_2 + t_1}{2} = \text{mean } t.$$

$R_2 - R_1$ = resistance difference corresponding to temperature difference $t_2 - t_1$.

Differentiating—

$$(4) \quad \Delta t = \frac{1}{R_0(a + 2BT)} \Delta R.$$

By the use of formula 4 a table of factors may be computed, values for R (mean) being assumed, so that differences in resistance as measured on the slide wire may be converted into temperature differences. Such a table, furnished by the Bureau of Standards with certificate of calibration of a resistance thermometer submitted to that bureau, is given below:

Conversion table for converting resistance to temperature.

Plug setting.	Factor.	Plug setting.	Factor.
26.6-----	9.901	27.6-----	9.930
26.7-----	9.904	27.7-----	9.933
26.8-----	9.907	27.8-----	9.936
26.9-----	9.910	27.9-----	9.939
27.0-----	9.913	28.0-----	9.942
27.1-----	9.916	28.1-----	9.945
27.2-----	9.919	28.2-----	9.948
27.3-----	9.922	28.3-----	9.951
27.4-----	9.924	28.4-----	9.954
27.5-----	9.927	28.5-----	9.957

^a Dickinson, H. C., and Mueller, E. F., New calorimetric resistance thermometers: Bureau of Standards, Bull. 4, vol. 9, October, 1913, pp. 483-492.

METHOD OF CALIBRATION.

In order to arrive at the relation between the resistance found and the temperature (hydrogen scale), it is necessary to know the resistance of 0° C., at 100° C., and at some intermediate point; for example, 32.384° C., the transition point of sodium sulphate. From the resistance interval ($R_{100}-R_0$) the so-called platinum temperature of the Calendar formula may be calculated, and from $R_{32.384}$ the wire constant S may be obtained. The following observations and calculations involved in the thermometer calibration will make the method clear:

Specimen record sheet showing results of calibrating a thermometer.

Instrument used:

Bridge No. 15749.

Coil (10 ohms) No. 5566.

Thermometer No. 26289.

Barometer No. 760.

Hypsometer No. 20.

Correction formula for barometer:

$$h_0 = h_t (1 - 0.000162t) 0.999462 \text{ (for Washington)};$$

Corrected resistance of thermometer in ice..... 25.2433

Corrected resistance of thermometer in steam..... 35.1092

Difference fundamental interval)..... 9.8659

Barometer reading at 24.8° C..... 753.7

Barometer reading corrected to standard conditions (B)..... 750.27

Corrected boiling point of water $= 100^{\circ} - 0.375 (76.0 - B)$

$$= 100^{\circ} - 0.375 (76.000 - 75.027).$$

$$= 99.635^{\circ} \text{ C.}$$

or 9.8659 ohms is the resistance interval corresponding to temperature interval 99.635° . Therefore, 9.902 ohms = resistance interval $0^{\circ} - 100^{\circ}$.

The resistance of the thermometer at the transition point of sodium sulphate (32.384° C.) was found to be 28.4816 ohms. The constant S may be obtained from the formula giving the so-called platinum temperature—

$$pt = \frac{R_t - R_0}{F} \times 100 = \frac{3.2384}{9.902} \times 100 = 32.704$$

By substitution in the formula—

$$t - pt = S \left(\frac{t}{100} - 1 \right) \frac{t}{100}.$$

Making the substitution:

$$32.384 - 32.704 = S \left(\frac{(32.384)^2}{(100)^2} - \frac{32.384}{100} \right)$$

From which $S = 1.46$.

Impurities in the sodium sulphate rendered the value 1.46 too low, the correct value for S being 1.48. Of course, if it were proposed to measure small temperature differences in the calorimeter, and error of this magnitude in S would have a negligible effect on the result.

If, however, absolute temperatures were wanted, such an error should not be overlooked.

The calculation of a temperature corresponding to an observed resistance will be clear from the following calculation based on the constants found above:

Suppose the observed resistance is 30.000 ohms. Then—

$$pt = \frac{30.000 - 25.2433}{9.902} = 48.038$$

$$t - 48.038 = 146 \left(\frac{t}{100} - 1 \right) \frac{t}{100}, \text{ or}$$

$$0.000146t^2 - 1.0146t + 48.038 = 0$$

$$t = 47.674^\circ \text{ C.}$$

As is shown presently, it is not necessary to apply the above formula in the determination of calorimeter temperatures, provided the calorimeter has been standardized by the combustion method.

DETERMINATION OF THE WATER VALUE OF THE CALORIMETER.

It is now rather generally recognized that the best methods for calorimeter calibration are as follows:

(1) Electrical method based on the input into the calorimetric system of a known amount of heat electrically.

(2) Calibration by burning substances of known heating value.

The electrical method is absolute, and, of course, is to be preferred for that reason. However, rather elaborate equipment is necessary, the manipulation requires considerable skill and time, and consequently the method is perhaps not well suited to the purposes of the commercial laboratory.

CALIBRATION BY COMBUSTION OF STANDARDS.

The method involving the burning of substances of known treating value leaves nothing to be desired in simplicity and is reliable provided one is sure of the heating value of the standard substance used. Fortunately, such standard substances may now be obtained from the Bureau of Standards.

To standardize a calorimeter by means of such standard substances it suffices to make six or eight combustions, sufficient amounts of the standard being used to produce about the average temperature rise obtained with coal. The factors are calculated from the results of the combustions, and the average value is taken for the calorimeter factor. Thus—

$$(WE + W)t - c = H \times a.$$

WE = water equivalent of calorimeter.

W = weight of water used.

t = corrected rise in temperature.

c = corrected HNO_3 formed.

H = heating value of standard substance per gram.

a = weight of standard substance used.

A specimen example in standardizing a calorimeter follows:

Specimen record in standardization of calorimeter.

Sample No. *Standard sample sucrose No. 17a, Bureau of Standards.* Date: *May 24, 1916.*

Weight of sucrose, grams..... 2
Weight of naphthalene, grams..... 0.02

Time.	Readings.				
2.17	0.710	1.743	4.293	5.903	6.101
2.18	.721				
2.19	.733				
2.20	.744				
2.21	.757	+ .0118	+ .0046		6.893
2.00½	2.500	+ .0068	+ .0016		.757
2.22	5.050	— .0005	— .0028		6.136
2.23	6.600	— .0051	— .0054		— .0134
2.24	6.858	— .0056	— .0057		2)6.1494
2.25	6.891	— .0057	— .0057		3.0747
2.26	6.893	— .0057	— .0196		
2.27	6.887	.0175	+ .0062		
2.28	6.883		— .0134		
2.29	6.878				
2.30	6.871				
2.31	6.895				
2.32	6.859				

Heat of combustion of 2 grams of sucrose, calories..... 7,898
Heat of combustion of 0.02 gram of naphthalene, calories..... 192.3

Titer, calories..... 17

8,107.3

$$\frac{8,107.3}{3.0747} = 2,636.7 = WE$$

Wire fuse=Platinum.

Titer, c. c.=3.4 (1 c. c.=5 cal.)=17.0 calories.

Bomb, No. 3.

Oxygen used, pounds=350.

Valve, O. K.

(Signed) E. L. W.

Obviously this method, besides being simple and easy of application, tends greatly to minimize constant errors. Such errors include change in specific heat of water, errors in cooling correction, thermometer, heat input from stirring, and others, whereas, with the electrical method, all measurements and calculations must be as nearly absolute as possible.

With empirical standardization of the calorimeter, it is not at all necessary to convert resistance readings of the bridge into temperature. In the previous discussion of formulas for converting resistance differences into temperature differences the assumption was made that for a given mean resistance the temperature-resistance curve is practically a straight line for small variations from the mean. The fact is that the error introduced by this assumption for a difference equal to the total range of the slide wire, if the plug settings remain untouched, is less than 0.002° C. With the bureau's calorimeters the range of a determination covers a little over half the extent of the slide wire, and the range covered in calibration is

the same as that actually used, so that any variations of the temperature-resistance curve are compensated within the limits of accuracy of the apparatus. A higher degree of accuracy is therefore obtained by empirical standardization without conversion than by absolute standardization with conversion. All thermometers have a fundamental interval of nearly 10 ohms. In view of the considerations mentioned—the bureau does not convert resistance into temperature—a comparison by combustion of a standard substance every few days being considered sufficiently accurate for all practical purposes. At the same time that the combustion comparison is made, the ice point of the thermometer is taken to insure that the indication of the thermometer or the calorimeter factor has not changed.

ELECTRICAL STANDARDIZATION.^a

Although standardization by the electrical method is not recommended when reliable combustion standards are available, an electrical method used by the authors is briefly discussed here.

APPARATUS NEEDED.

If the best results are to be obtained with the electrical method there should be available (1) a good potentiometer outfit and a standard low-resistance coil for current measurement and measurement of potential drop across the heating coil when the current is passing; (2) storage batteries to provide current at constant voltage; (3) a chronometer and some sort of automatic switch for directing the current; (4) a resistance thermometer for measuring the temperature rise in the calorimeter due to the heat input; and (5) a heating coil of low heat capacity and containing a minimum amount of insulating material. The constants of all apparatus used should, of course, be accurately known.

The authors did not possess storage-battery equipment of sufficient capacity, and they soon found that it was impossible to measure the current input by potential drop across a standard coil, owing to the variations in voltage at the laboratory power terminals. Accordingly, in the actual experiment, the current was measured by means of a large voltmeter of the Bureau of Standards type, placed in series with the heating coil, the resistance of which was determined for conditions of the experiment. The heating coil was made of No. 24 double silk covered manganin wire of approximately 10 ohms resistance. The wire was wound in spiral and drawn over a thin glass tube bent in a circle. The coil and tube were then given a thin coating of shellac and baked at 150° C. for several hours. Copper ter-

^a Dickinson, H. C., Combustion calorimetry and the heats of combustion of cane sugar, benzoic acid, and naphthalene: Bureau of Standards, Bull. 2, vol. 11, Mar. 1, 1915, pp. 189-257.

minals were then soldered on, and the whole coil was given a thin coating of paraffin and attached to the calorimeter lid.

The equipment is shown in figure 9. *A* is the calorimeter (in this experiment a Williams instrument not equipped for temperature control of the jacket), *C* is the resistance thermometer bulb, *D* is the voltameter, *E* is a double-pole magnetic switch with contacts amalgamated and covered with mercury and oil. This switch is controlled by the timer *G* through the telegraph relay *F* and the hand-operated

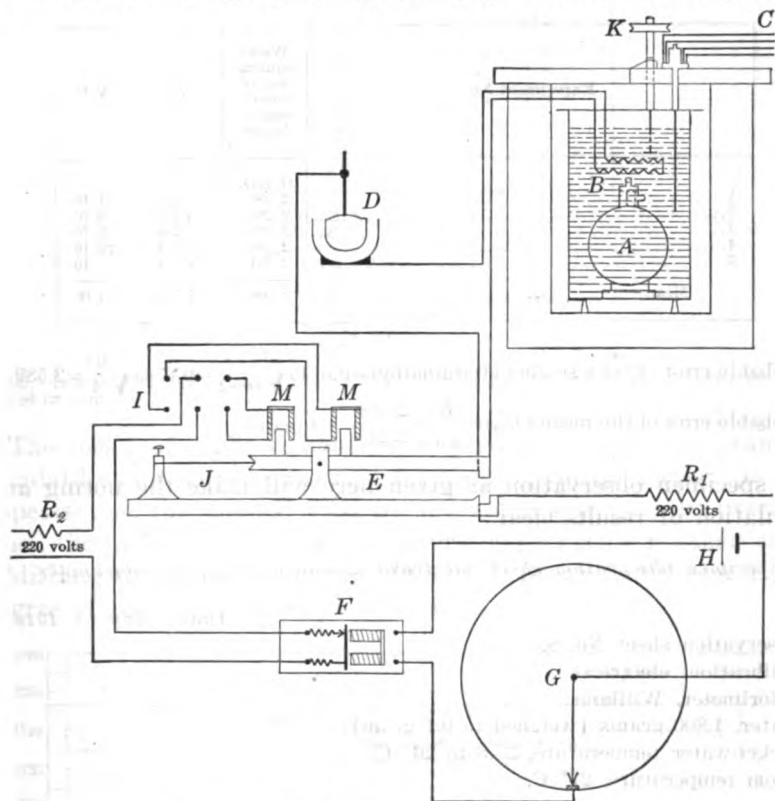


FIGURE 9.—Apparatus for electrical calibration.

double-throw switch *I*. At *J* is shown a flat spring the function of which is to hold the switch open or closed.

The resistance of the heating coil was carefully determined at 20° C., and then a correction was applied for increase in resistance through the passage of the heating current. In order to obtain this correction a copper-constantin couple was placed in close contact with the heating coil, and the increase in temperature from the passage of current was noted. The resistance of the coil was calculated by the formula $R = R_{20} (1 + 0.000023 (15))$. The resistance of the lead from the voltameter cathode to the coil was determined, and an appropriate correction was applied.

RESULTS OF STANDARDIZATION TESTS.

In order that the results should be comparable with combustion standardization results made with the same calorimeter, combustion results were obtained with the heating coil in place and with the same temperatures as with the electrical standardization. The results of five experiments are as follows:

Results of standardization tests of calorimeter.

Experiment No.	Water equivalent of calorimeter factor.	V.	V. ²
1.....	2,286	-4.6	21.16
2.....	2,292	+2.6	6.76
3.....	2,288	-2.6	6.76
4.....	2,296	+5.4	29.16
5.....	2,291	+ .4	.16
Mean.....	2,290.6	EV =	64.00

Probable error (R) of a single determination $= 0.6745 \sqrt{\frac{V^2}{n-1}} = 0.6745 \sqrt{\frac{64}{4}} = 2.589$.

Probable error of the mean (R_m) $= \frac{R}{\sqrt{n}} = \frac{2.598}{2.23} = 1.1$ gram.

A specimen observation as given here will make the noting and calculation of results clear:

Specimen observation sheet, electrical standardization of calorimeter.

Date: May 12, 1916.

Observation sheet No. 8.

Calibration, electrical.

Calorimeter, Williams.

Water, 1,800 grams (weighed to 0.1 gram).

Jacket-water temperature, 25.8 to 26° C.

Room temperature, 27° C.

Heat input:

Resistance of coil, 10.425 ohms (corrected).

Time, 120 seconds.

(Ag. deposited in one ampere-second taken as 0.0011163 gram.)

Weight of kathode, plus deposit, 91.0417 grams.

Weight of kathode, 90.3409

Weight of deposit, 0.7008

$$\frac{0.7008}{0.0011163 \times 120} = 5.231 \text{ amperes, average current (amps).}$$

Heat input $= H = 0.2391 I^2 R t = 0.2391 (5.231)^2 (10.425) (120) = 8188.7$ calories.

Specimen sheet showing calorimeter temperatures, electrical standardization of calorimeter.

Time, minutes.	Reading, ° C.	
31	23.360	
32	23.369	
33	23.376	
34	23.383	
35 (a)	23.392	$r_1 = +0.0080$
35½	24.120	+ .0058 > +0.0034
36	25.130	+ .0028 > + .0021
37	26.895	- .0026 > + .0001
38	27.011	- .0028 > - .0027
39	26.979	- .0028 > - .0028
40 (b)	26.972	$r_2 = - .0028 > - .0028$
41	26.969	$\Sigma = - .0027$
42	26.964	
43	26.961	
44	26.959	
45	26.958	

26.972 (b)
23.392 (a)

3.580 = rise.
.0027 = cooling correction.
.008 = thermometer correction.
3.5747 = corrected rise.
8188.7
3.5747 = 2290.7

Note.—Length of heating period (a to b) same as that in combustion experiments, no correction being applied for bomb lag.

The mean of eight combustion experiments with 0.85 gram of standard naphthaline^a gave 2291 for the value of the factor. It thus appears that the method used by the authors is entirely practical when the mean of the results of several experiments is taken as establishing the value sought, and that with better facilities a higher degree of accuracy would be obtainable.

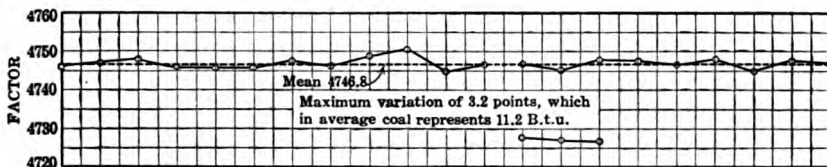


FIGURE 10.—Curve showing variation in factor for bomb No. 3. Single determinations, three determinations per month for 8 months. Naphthalene used, Bureau of Standards No. 35 (certified 9,622 (20°) calories per gram). Rise in temperature $\times$ factor = B. t. u.

The slight variation of the factor of bomb No. 3 during a period of eight months is shown in Fig. 10.

EASY MANIPULATION OF RESISTANCE THERMOMETER.

One objection made to the resistance thermometer is that its manipulation is cumbersome. However, the authors have found that it

^a Certified sample (9,610 calories a gram at 10° C., Bureau of Standards sample No. 35).

is fully as convenient to make the necessary adjustments and readings with this instrument as to follow the indications of the mercury thermometer. It is only necessary to follow approximately the rise in temperature during the combustion period; for that purpose a bridge key of high resistance can be provided to prevent excessive current going through the galvanometer when the bridge is considerably out of balance. A key with zero resistance in series is, of course, used when the temperature change becomes slow and temperatures must be read closely.

RESULTS WITH BUREAU'S MERCURY THERMOMETER.

As regards the comparison of the mercury thermometer with the platinum resistance thermometer, the following results obtained with mercury thermometers in the bureau's laboratory at its Pittsburgh, Pa., experiment station have been furnished by A. C. Fieldner,^a chemist, in charge of the laboratory. The calorimeter buckets used at the Pittsburgh laboratory do not have floating covers. The standardization and all determinations were made with the temperature of the bucket below that of the jacket before and after the end of a determination, evaporation errors being prevented by having the space surrounding the bucket saturated with water vapor.

Data on results with mercury thermometers.

Date of determination.	Value, calories.	Residual, v.	V^2 .
June 7.....	6321.6	+0.5	0.25
June 12.....	6321.2	+ .1	.01
June 22.....	6320.8	- .3	.09
June 30.....	6319.7	- .14	1.96
June 30.....	6319.0	-2.1	2.31
July 10.....	6321.0	- .1	.01
July 17.....	6327.7	+6.6	43.56
July 25.....	6317.5	-3.5	12.25
Aug. 1.....	6321.8	+ .7	.49
Aug. 14.....	6320.4	- .7	.49
Mean.....	6321.1		61.42

$$r=0.6745\sqrt{\frac{61.42}{9}}=1.75$$

1.75 calories=3.2 B. t. u., probable error.

This table shows that the probable error obtained with the use of the mercury thermometer is identical with that obtained in the values submitted in the table on page 45.

^a Personal communication.

PERFORMANCE OF THE CALORIMETER.

ATTAINABLE RAPIDITY.

Expectations in regard to rapidity have been fully realized, for a skillful manipulator can average 35 determinations a day or approximately twice the number possible with the old form of apparatus. The time required for an observation with the old calorimeters was 15 to 18 minutes, whereas 8 minutes suffices with the calorimeters now used. Manipulation of the bomb is simplified by dispensing with wrenches (except for closing) and by using the quarter-turn sealing nut instead of the long threaded nut usually employed. In fact, great care has been given all details tending to facilitate manipulation, useless motions being eliminated and simple motions serving for several functions. In this way the cost of making an analysis has been reduced somewhat. This final point deserves consideration, for the material analyzed is relatively cheap and the cost of analysis must be kept below the value of the resulting gain.

CONSTANCY OF JACKET.

The constancy of temperature of the jacket water in the calorimeter tank is shown by the curves of figure 11. Curve 1 was plotted from readings with a mercury thermometer placed in the bath at the point where the water enters the stirrer tube, that being one of the points of greatest agitation, and the thermometer was read to 0.001° C. by means of cathetometer. Curves 2 and 3 were plotted from readings obtained with two different resistance thermometers, the readings being in 0.1 and fractions of 0.1 ohm resistance difference from the bridge setting. To reduce temperature differences, as expressed in ohms, to degrees centigrade, the difference in ohms is divided by 2. The two series of readings were obtained under the same conditions, and the thermometers were placed at opposite sides of the tank near the calorimeters with which they were ordinarily used. The times of reading, however, do not coincide for these two curves. It will be noted that the period of curve 1 is longer than that of curves 2 and 3. This is because the room temperature was nearer the thermostat setting for curve 1. The effect of temperature variations of the magnitude shown by these curves on the heat distribution in the calorimeter may be calculated (the magnitude of the various lugs involved being known) from the integrals of the error curve and the heat transfer curve of the calorimeter, by the formula $\frac{d\theta}{dt} = f(t) - K(\theta - \theta_e)$, in which θ is the temperature of the calorimeter, θ_e the temperature of the jacket, $f(t)$ the rate of temperature charge, and K a constant.

The error curve may obviously be determined closely for given conditions by Fourier's method. A good idea of the effect of the variation curve, however, may be gained from the following considerations: As will presently be shown, the heat input into the calorimeter system resulting from a 2° difference (approximately the actual difference at the beginning of combustion) is 14.9 calories per minute, and the output at the end of the combustion period is about the same. Now, if it be assumed that the maximum variation of the tank-water temperature is $\pm 0.014^\circ \text{C.}$, and that the error

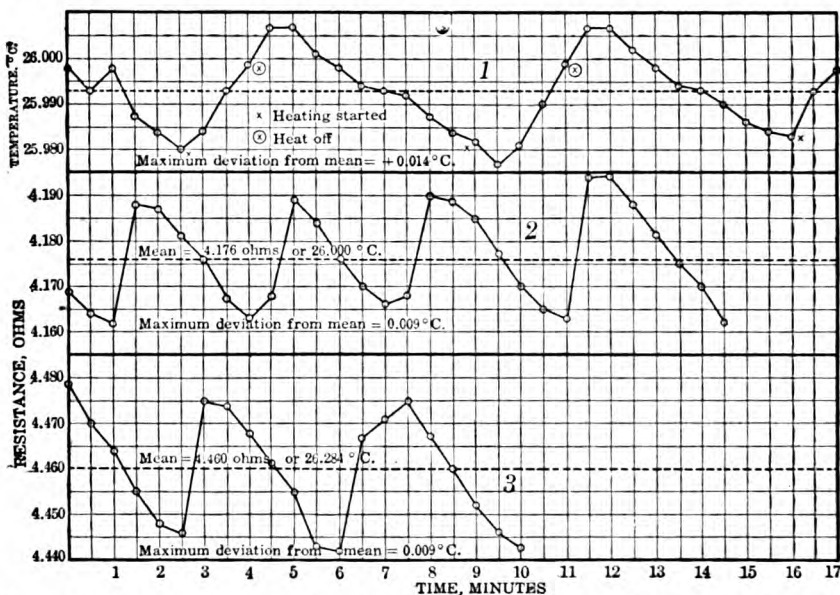


FIGURE 11.—Curves showing extent of temperature variations in jacket water in calorimeter tank. No. 1, read with mercury thermometer at periods of approximately 4 minutes. Nos. 2 and 3, read with resistance thermometer at periods of approximately 3 minutes.

curve at opposite inflection points coincides with the heat transfer curve at its inflection points, the maximum error that can result is obtained thus:

$$\text{Maximum error} = 2x, \text{ where } \frac{14.9}{2^\circ} = \frac{x}{2.014}, \text{ whence } x = 0.1 \text{ and } 2x = 0.2 \text{ calories.}$$

$14.9 + X$ = heat transfer due to 2.014° temperature difference, approximately, or 0.2 calories per minute contact at each point.

Thus, the effect is negligible. It was determined that the variation curves for other parts of the tank were the same as shown above; however, as would be expected, the curves differ slightly in phase, owing to greater lag at some points than at others.

RATE OF COMBUSTION IN THE CALORIMETER.

Obviously the shape of the combustion curve will be affected somewhat by the time taken to complete the combustion reaction, and in

order to obtain reliable data on the time required for this reaction the authors devised the following experiments:

Combustions were made in an old Emerson calorimeter, 500 c. c. capacity, which was provided with a heavy glass window for transmitting the light from the combustion. A mirror was so placed at an angle with the window that the time of evolution of light from the combustion could be observed without danger to the observer from possible fracture of the window; the results were as follows:

Results of combustions, Emerson Calorimeter.

Substance.	Pressure, pounds.	Time, seconds.
Bituminous coal.....	350	47
Do.....	350	42
Lignite.....	350	23
Anthracite.....	350	75
Naphthaline, 0.85 gram.....	350	40
Semibituminous coal.....	175	110
Do.....	200	110
Do.....	375	45
Do.....	475	25
Do.....	575	19

The difference in the results obtained at constant pressure for lignite and for anthracite may be taken as about covering the range of variation in time required for combustion of the substances except liquid and gaseous fuels tested in fuel calorimetry. The effect of a slow rate of combustion, that is, one slower than the rate during calibration, is to change the shape of the combustion curve, as the total time required to establish equilibrium is not greatly increased by a slow combustion rate. The time $t_n - t_o$ (see fig. 12), however, will be considerably increased, since $\frac{d\theta}{dt}$ is large during this period.

The net effect of variation in combustion rates through variation in pressure is best determined by experiment. Accordingly, two groups of determinations for the same semibituminous coal were made, one group at 200 pounds pressure and one group at 450 pounds. As the average results of the two groups indicate, the cooling correction determined by the Bureau of Mines method is considerably larger for the high pressure, whereas the interval $\theta_2 - \theta_0$ is about the same.

Relation of pressure to rate of combustion.

Pressure.	Correction.	$\theta_2 - \theta_0$	Rise, tenths of an ohm.
200 lbs.....	0.0156	6.249	3.1323
450 pounds.....	.0209	6.248	3.1345
Difference.....	$\frac{.0053}{2} = .0026$	$\frac{.001}{2} = .0005$	.0022

Approximately the difference is about 10 B. t. u. for factor 4742. The table above shows that this corresponds to a variation in combustion time of 70 seconds minus 25 seconds—that is, 45 seconds—or nearly 300 per cent.

It would seem that the error introduced in the determination of heating value of substances having a lower combustion rate than the calibration substance might be offset by using higher oxygen pressures. Thus, if it be assumed that the conductivity of the gas layer varies directly as the pressure and that a given amount of heat is liberated by the standard 0.85 gram of naphthalene (which has about the same combustion rate as 1 gram of semibituminous coal), then a weight of anthracite coal liberating the same amount of heat should be burned at approximately $350 + 175 = 525$ pounds. The application of this method would, of course, entail extra work. The results can be only an approximation, and perhaps the method would not be justified in routine work, as the variation involved is small.

THE COOLING CORRECTION.

Most methods for the calculation of the cooling correction are based on Newton's law of cooling, which states that $\frac{dT}{dt} = C(T - T_0)$, where $T - T_0$ is the temperature difference, C is a constant and t is the time applied to the calorimetric determination. The complete differential equation takes the form $\frac{dT}{dt} = C(T - T_0) + f(t)$ where $f(t)$ relates to the rate of energy supply, and $C(T - T_0)$ relates to the cooling correction, T_0 being taken as the temperature of the jacket which is assumed constant. Now, on the assumption that $T = 0$ when $f(t) = 0$, at time 0, the solution of the equation above is $T = T_0(1 - e^{-ct}) + \int_0^t f(t) c$ being assumed constant. However, this is not necessarily true, unless certain conditions are fulfilled.* The cooling correction then would take the form

$$T' \left[1 - e^{-ct} \right]_0^t - T'' \left[1 - e^{-ct} \right]_0^t$$

where $T' = T_n - T_0$ and $T'' = T_2 - T_n$, T_n being the temperature (determined by experiment) at which there is no heat exchange between the jacket and calorimeter. Figure 12 shows the results of this method applied to a combustion of naphthalene, the constant C having been determined experimentally. The differential resistance as plotted (direct readings on the bridge wire) divided by 2 is very nearly equal to degrees centigrade, and the cooling correction (0.00685° C. , additive) is small.

* Dickinson, H. C., Combustion calorimetry and the heats of combustion of cane sugar, benzoic acid, and naphthalene: Bu. Standards Bull. 2, vol. 11, Mar. 1, 1915, pp. 189-257.

The method regularly employed by the Bureau of Mines for calculating the cooling correction may be illustrated by applying it to

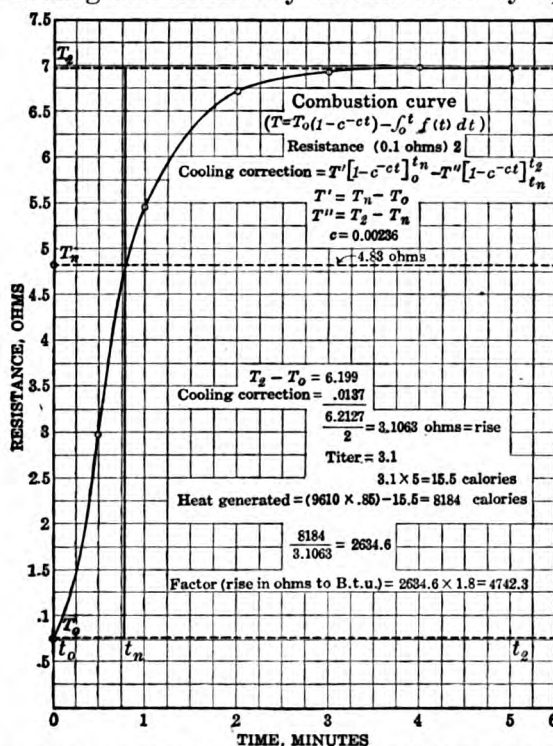


FIGURE 12.—Combustion curve for naphthalene from results with bomb No. 3. Charge, 0.85 gram naphthalene.

the combustion experiment given above. The observation sheet is as follows:

Specimen calorimeter sheet.

Standard naphthalene, 0.85 grams. Date: Dec. 10, 1915.

Time.		
11.33	0.713	2.198, 4.688, 5.948, = $t_0 - t_1, \dots, t_{(n-1)}$, combustion period.
11.34	.724	
11.35	.738	
11.36	.748	
11.37	.761	
11.38	.772 + .0118 + .0043	6.971
11.4	2.970 + .0055 + .0009	0.772
11.39	5.460 - .0018 - .0036	6.199
11.40	6.720 - .0054 - .0057	-.0163 = cooling correction
11.41	6.938 - .0061 - .0061	2 6.2153
11.42	6.970 - .0061 - .0061	3.1077 = corrected rise in °C.
11.43	6.971 - .0061 - .0215	
11.44	6.962 0179 + .0052	
11.45	6.956	
11.46	6.950	
11.47	6.945	
11.48	6.939	
11.49	6.933	
11.50	6.928	

NOTE.—Cooling correction by Dickenson's method would be -.0167.

Titer = 3.1 cc. Bomb No. 3.

(Signed) E. L. W.

The sum of the initial rate, r_1 , and the final rate, r_2 , given as 0.0179, represents the total change of rate for the combustion period. Now, assuming Newton's law to hold, then

$$\frac{r_1 + r_2}{A} = \frac{x}{T}$$

Where T is any temperature interval during the combustion period and x is the corresponding rate change at that time

$$\text{Then } \frac{r_1 + (r_1 - x_1)}{4} + \frac{r_1 + (r_1 - x_2)}{4} + \frac{r_1 + (r_1 - x_3)}{2} + \frac{x_{(n-1)} + r_2}{2} = \text{cooling correction.}$$

The first two terms are for half-minute interval observations. The reader should note that r_1 and r_2 are not strictly the rates at the beginning and end of the combustion period represented; however, the error introduced by considering them as such is less than the experimental error of their determination.

Applying Dickinson's^a method to the calculation of this curve where

$$C = a \int_0^{t_m} (\theta_n - \theta_0) dt + a \int_0^{t_2} (\theta_2 - \theta_0) dt$$

or

$$C = r_1 (t_m - t_0) + r_2 (t_2 - t_m)$$

where t_m is taken as t_n at the point of 77 per cent of the total rise instead of 60 per cent, giving $0.0118 (0.77) - 0.0061 (4.23) = 0.0091 - 0.0258 = 0.0167$, which agrees well with the figures found above.

Now, it has been noted that there is quite a little variation in the cooling correction obtained for different combustions with the same amount of heat liberated, even when the initial and final temperatures of the combustion period are the same, because of the difficulty of getting exact temperature readings during the first part of the combustion period. Accordingly, the average correction obtained for 5 to 8 combustions (the beginning temperature always remaining the same) of the same weight of standard has been taken as the correction corresponding to that rise. A table of corrections may be obtained from the results of combustion of different weights of standard corresponding to different resistance differences (rises). Such a table for bomb 3 is given below.

Since the amount of heat liberated in the bomb and the rate of combustion of various coals will not vary greatly, the error involved by assuming the time constant for the period is slight, and it becomes necessary to make only two observations, the initial and final, for a determination, the cooling correction being noted from the table.

^a Dickinson, H. C., Combustion calorimetry and the heats of combustion of cane sugar, benzoic acid, and naphthalene: Bureau of Standards, Bull. 2, vol. 11, Mar. 1, 1915, pp. 189-257.

Table of corrections for bomb No. 3.

Rise.	Correction.	Rise.	Correction.	Rise.	Correction.
6.40	-0.0175	5.85	-0.0106	5.30	-0.0043
6.35	-.0104	5.80	-.0101	5.25	-.0037
6.30	-.0158	5.75	-.0095	5.20	-.0031
6.25	-.0153	5.70	-.0089	5.15	-.0025
6.20	-.0147	5.65	-.0083	5.10	-.0020
6.15	-.0141	5.60	-.0078	5.05	-.0015
6.10	-.0135	5.55	-.0072	5.00	-.0008
6.05	-.0129	5.50	-.0066	4.95	-.0003
6.00	-.0123	5.45	-.0060	4.90	-.0003
5.95	-.0118	5.40	-.0055	4.85	-.0009
5.90	-.0112	5.35	-.0048		

Example: $\begin{matrix} 5.95 \\ - .0118 \\ \hline 5.9618 \end{matrix}$
 $2.9809 = .29809 \text{ ohms.}$

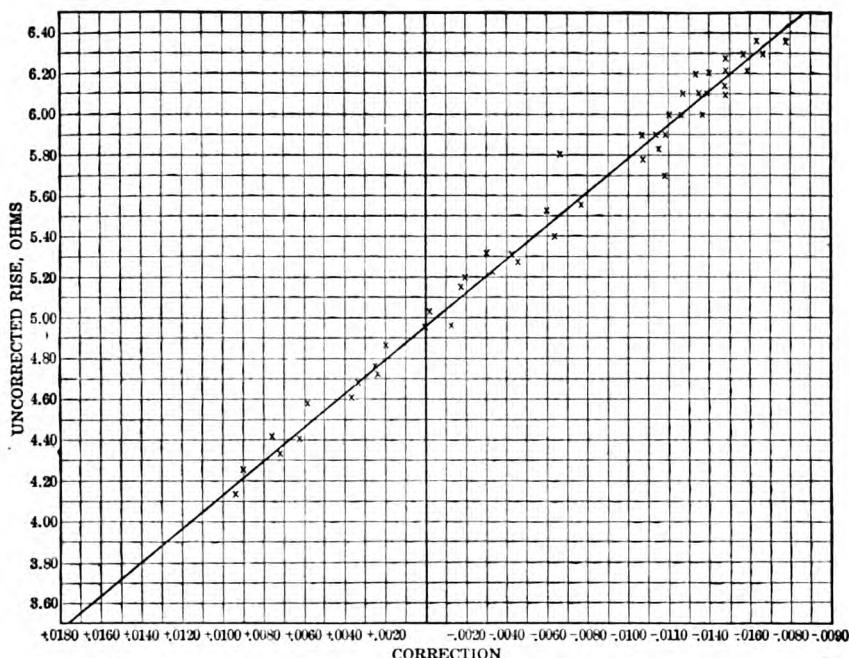


FIGURE 13.—Curves showing radiation corrections for bomb No. 3.

The radiation corrections for bomb No. 3, as established by the method mentioned, are represented in figure 13 by the straight line. The different observations plotted in the figure show the variations from the straight line due to difference in rate of combustion of different coals.

EFFECT OF EVAPORATION.

As the temperature of the calorimeter with respect to that of the jacket changes from negative to positive during a combustion, if the calorimeter is not sealed, water will evaporate from the exposed

surface and condense on the cooler walls of the jacket when the temperature of the calorimeter is positive. Thus an amount of heat proportional to the amount of water evaporated is carried from the calorimeter system. That the weight of water evaporated is about proportional to the time for a given temperature difference with the bureau's calorimeters has been shown by making a number of combustions with the water seal removed. Thus, for a difference of approximately 1.5°C . the normal rate of temperature drop is $0.0045-0.0050$ (corresponding to $0.0022^{\circ}-0.0025^{\circ}\text{C}$.) per minute, while with the seal removed the figure was found to be 0.0035° per minute.

It would seem that serious error would not be introduced by dispensing with the seal as long as combustion standardization is performed under the same conditions or as long as the calorimeter temperature is always below the jacket temperature. The apparent cooling correction would, of course, be larger because of the evaporation factor, and in that respect would be subject to larger error. For this reason alone the seal is perhaps justified, as it involves little added expense and does not affect in the least the manipulation of the instrument. The calorimeter must be perfectly dry when placed in the jacket or an uncertain evaporation factor will be introduced. This factor will be larger than that just mentioned because of the larger surface exposed and will be uncertain because the excess moisture may all have evaporated during the combustion period, causing an abrupt change in the heat transfer equilibrium. Such a condition exists when the water charged into the calorimeter is below the dew point of the atmosphere of the room; then a considerable amount of moisture will deposit on the calorimeter can before this is placed on the jacket. On numerous occasions the authors have found erratic results due to this cause, and for the past year working temperatures have been kept well above the dew point. Now, if the jacket walls are not kept dry, water will distill to the calorimeter, causing an input of heat while the calorimeter temperature is negative and an outflow of heat when the calorimeter temperature changes to positive. Hence, it is considered much better practice to work well above the dew point, with calorimeter and jacket surfaces dry, than to permit evaporation and attempt to correct for it.

ACCURACY ATTAINABLE WITH THE CALORIMETER.

The probable error of a single determination with bomb No. 3 of the equipment described may be taken as established by the following series of experiments:

Results establishing the heating-value error, from 24 determinations with the same bottle sample of 100 grams.

Date of determination.	Value.	Residual v.	r ² .
1914.	<i>B. t. u.</i>	<i>B. t. u.</i>	
Jan. 22.....	14,651	5	25
Jan. 24.....	14,639	-7	49
Jan. 26.....	14,644	-2	4
Jan. 27.....	14,653	7	49
Jan. 28.....	14,648	2	4
Jan. 29.....	14,649	3	9
Jan. 30.....	14,646	0	0
Feb. 2.....	14,649	3	9
Feb. 3.....	14,649	3	9
Feb. 4.....	14,639	-7	49
Feb. 5.....	14,644	-2	4
Feb. 6.....	14,648	2	4
Feb. 7.....	14,639	-7	49
Feb. 9.....	14,641	-5	25
Feb. 11.....	14,653	-7	49
Feb. 12.....	14,651	-5	25
Feb. 13.....	14,644	-2	5
Feb. 14.....	14,653	-7	49
Feb. 16.....	14,644	-2	4
Feb. 17.....	14,644	-2	4
Feb. 18.....	14,651	5	25
Feb. 19.....	14,644	-2	4
Feb. 20.....	14,639	-7	49
Feb. 24.....	14,639	-7	49
Mean.....	14,646		551

$$r = 0.6745 \sqrt{\frac{\sum v^2}{n-1}} = 3.2 \text{ B. t. u.}$$

$$u = 4.9r = 15.7 \text{ B. t. u.}$$

As is indicated, the probable error with this particular coal is only 3.2 B. t. u. The coal used must be regarded as of constant heating value, for, there being no noticeable regular variations in the heating value during the period covered by the experiment, the sampling must have been uniform, and there was no appreciable moisture change. In other words, the authors might as well have been working with a standard combustible, and the order of accuracy obtained represents that of which the apparatus itself is capable. With other coals the problem is obviously different for these reasons: (1) If the sample is difficult to mix thoroughly, there may easily be an error of 0.1 per cent introduced by variations in the nature of the impurities weighed; (2) 0.1 or 0.2 per cent error may be introduced by a change in moisture content during the time between the moisture and calorimeter determinations; (3) some change may be caused by the varying amounts of gases held by the coal.

The authors sought to gain information on the last point by exposing a sample of coal of known heating value in atmospheres of various gases, and afterwards determining its heating value. The sample (1 gram) was weighed into a calorimeter tray and placed in a desiccator, then the air in the dessicator was exhausted. The gas under test was then allowed to enter the desiccator to atmospheric pressure; the coal, after remaining for about one-half hour in the

calorimeter, was removed, and its heating value was determined. Hydrogen and producer gas containing a high percentage of illuminants were tried. No appreciable change could be noted for the hydrogen, but the producer gas gave consistently higher results, showing that with even such short exposure some gases would be absorbed sufficiently to introduce appreciable error. Also it is conceivable that the coal during the short time needed for crushing and sampling may lose gas enough to cause appreciable error. Such loss, however, relates to the treatment of the sample before analysis and affects the calorimeter determinations indirectly.

IMPORTANT ADVANTAGES OF THE EQUIPMENT.

Although few other laboratories probably require a calorimeter outfit of such large capacity as that used by the Bureau of Mines, the method might well be employed with two or more units. One chemist can manipulate two calorimeter units advantageously by using the same bridge outfit for both, two thermometer bulbs and a mercury link switch being required. As it takes about six minutes for the calorimeter temperature to reach equilibrium after the firing of a charge, the chemist has time to set up another calorimeter during the interval, and by working two instruments in rotation will be able to turn out nearly twice as much work as he could with one. A further advantage to be gained through using more than one calorimeter is the facility for cross checking results. Occasionally one calorimeter gives erroneous results through a leak, faulty electrical insulation, binding of the stirrer, or some other common but not readily detected cause, but the chance is remote that two calorimeters will be out of order at the same time. For this reason, it has always been the practice in the Bureau of Mines laboratory to cross check all duplicate determinations with instruments that have been independently standardized. Of course the results are not as uniform as those obtainable with one instrument, for calibration errors are included when two instruments are used.

COST OF THE APPARATUS.

The cost per unit of the apparatus described in this paper was about the same as that of apparatus with the porcelain-lined bomb that may be purchased through chemical supply houses. Should the Bureau of Mines construct another such equipment, however, the cost could doubtless be much reduced, since the bureau now has all the special tools needed. The cost of the gold plating was approximately \$40 a bomb, and although replating has not been necessary, this work may be readily done in the laboratory at any time. As can be appreciated, this is a real advantage. Obviously the cost of the equipment

described could be somewhat reduced by substituting wood or metal for the stone tank; in fact, almost any sort of open water-bath might be used, and iron might replace brass as material for some of the parts. However, as the work, rather than the material, is the big item in cost, this last point is perhaps not important.

SERVICE OBTAINED.

Approximately 40,000 combustions have been made in the bureau's bombs, and as yet they show little wear. The lock nuts on two of the bombs have been renewed, the old ones having been strained by exerting too strong pressure with the wrench in closing. Two or three sets of valves have worn out, and electric plugs have given some trouble. In the authors' experience, valves and plugs are weak points in most commercial bombs, no valve or plug that is durable as compared with the rest of the apparatus being obtainable.

All things considered, the calorimetric outfit described in this paper has given considerably longer service than any with which the authors have had experience, and it is certainly more convenient to manipulate. One chemist can turn out almost twice as much work with it as with the usual form of apparatus.

PUBLICATIONS ON THE COMPOSITION OF COAL.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications can not be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines.

The Bureau of Mines issues a list showing all its publications available for free distribution as well as those obtainable only from the Superintendent of Documents, Government Printing Office, on payment of the price of printing. Interested persons should apply to the Director, Bureau of Mines, for a copy of the latest list.

PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

BULLETIN 28. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 51 pp.

BULLETIN 85. Analyses of mine and car samples of coal collected in the fiscal years 1911 to 1913, by A. C. Fieldner, H. I. Smith, A. H. Fay, and Samuel Sanford. 1914. 444 pp., 2 figs.

BULLETIN 116. Methods of sampling delivered coal, and specifications for the purchase of coal for the Government, by G. S. Pope. 1916. 64 pp., 5 pls., 2 figs.

BULLETIN 119. Analyses of coals purchased by the Government during the fiscal years 1900-1915, by G. S. Pope. 1916. 118 pp.

TECHNICAL PAPER 2. The escape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp., 1 fig.

TECHNICAL PAPER 5. Constituents of coal soluble in phenol, by J. C. W. Frazier and E. J. Hoffman. 1912. 20 pp., 1 pl.

TECHNICAL PAPER 8. Methods of analyzing coal and coke, by F. M. Stanton and A. C. Fieldner. 1913. 42 pp., 12 figs.

TECHNICAL PAPER 16. Deterioration and spontaneous heating of coal in storage, a preliminary report, by H. C. Porter and F. K. Ovitz. 1912. 14 pp.

TECHNICAL PAPER 35. Weathering of the Pittsburgh coal bed at the experimental mine near Bruceton, Pa., by H. C. Porter and A. C. Fieldner. 1914. 35 pp., 14 figs.

TECHNICAL PAPER 64. The determination of nitrogen in coal, a comparison of various modifications of the Kjeldahl method with the Dumas method, by A. C. Fieldner and C. A. Taylor. 1915. 25 pp., 5 figs.

TECHNICAL PAPER 76. Notes on the sampling and analysis of coal, by A. C. Fieldner. 1914. 59 pp., 6 figs.

TECHNICAL PAPER 113. Some properties of the water in coal, by H. C. Porter and O. C. Ralston. 1916. 30 pp., 3 figs.

TECHNICAL PAPER 140. The primary volatile products of the carbonization of coal; a sequel to Bulletin 1, The volatile matter of coal, by G. B. Taylor and H. C. Porter. 1916. 59 pp., 1 pl., 25 figs.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910. 56 pp., 1 pl., 9 figs. 10 cents.

BULLETIN 11. The purchase of coal by the Government under specifications, with analyses of coal delivered for the fiscal year 1908-9, by G. S. Pope. 80 pp. 10 cents.

BULLETIN 22. Analyses of coals in the United States, with descriptions of mine and field samples collected between July 1, 1904, and June 30, 1910, by N. W. Lord, with chapters by J. A. Holmes, F. M. Stanton, A. C. Fieldner, and Samuel Sanford. 1912. Part I, Analyses, pp. 1-321; Part II, Descriptions of samples, pp. 321-1129. 65 cents.

BULLETIN 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. 20 cents.

BULLETIN 38. The origin of coal, by David White and Reinhardt Thiessen, with a chapter on the formation of peat, by C. A. Davis. 1913. 390 pp., 54 pls. 80 cents.

BULLETIN 41. Government coal purchases under specifications, with analyses for the fiscal year 1909-10, by G. S. Pope, with a chapter on the fuel-inspection laboratory of the Bureau of Mines, by J. D. Davis. 1912. 97 pp., 3 pls., 9 figs. 15 cents.

BULLETIN 63. Sampling coal deliveries and types of Government specifications for the purchase of coal, by G. S. Pope. 1913. 68 pp., 4 pls., 3 figs. 10 cents.

TECHNICAL PAPER 65. A study of the oxidation of coal, by H. C. Porter. 1914. 30 pp., 12 figs. 5 cents.

TECHNICAL PAPER 93. Graphic studies of ultimate analyses of coals, by O. C. Ralston, with a preface by H. C. Porter. 1915. 41 pp., 3 pls., 6 figs. 10 cents.

